REMOVAL OF AMMONIA COMPOUND FROM WATER USING NANO AND MICRO CARBON MATERIALS

BY

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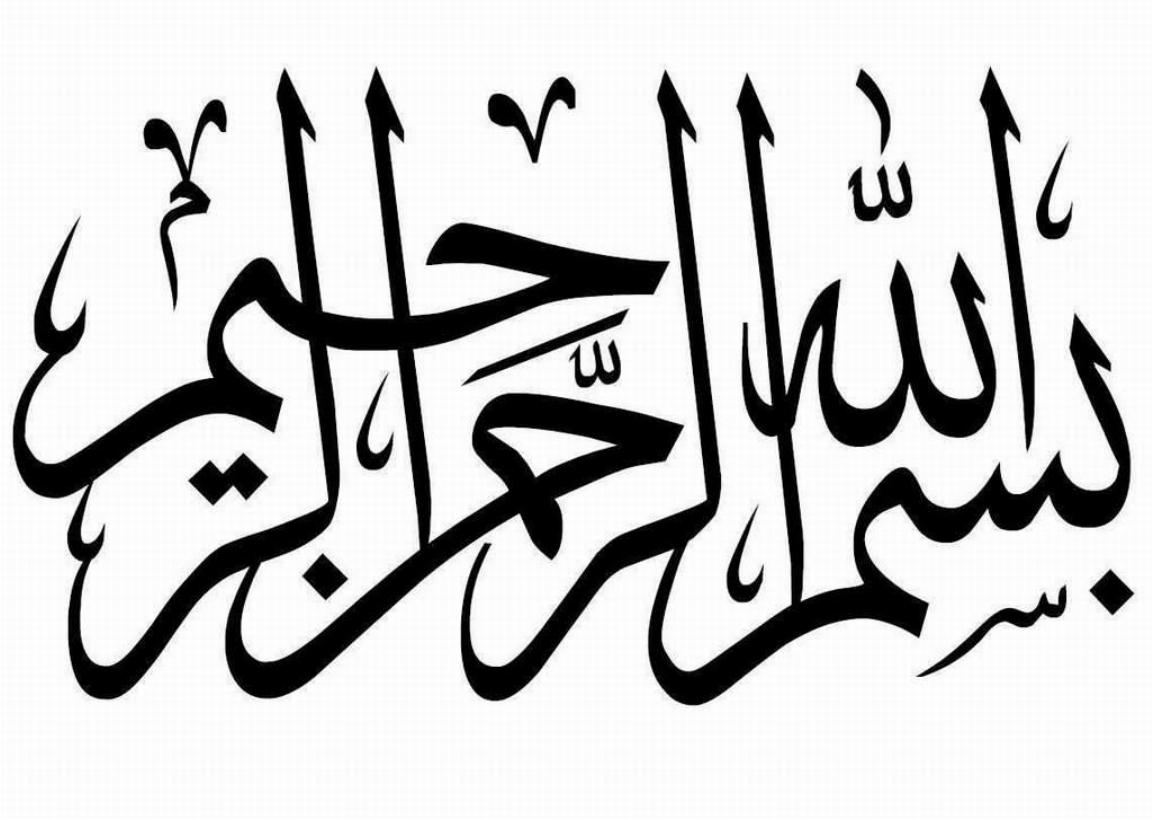
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DEDICATION

This work is dedicated to my beloved Parents, my brother and my sisters

ACKNOWLEDGMENTS

In the name of Allah, the most Beneficent, the most Merciful.

All praises be to Allah, and the peace and blessings of Allah be upon his prophet,

Mohammad (S.A.W)

I really want to give my deepest gratitude to all my thesis Committee members for all the support they provided me during my research work. Special thanks to committee chairman, **Dr. Basim Ahmed Abussaud**, and **Dr. Muataz Ali Atieh** for their special support and day to day guidance during the entire development phase of this study. I also want to thank all other committee members, **Dr. Nadir Al-Baghli, Dr. Halim Redhwi and Dr. Zuhair Malaibari** for their constructive guidance, valuable advices and cooperation.

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LIST OF ABBREVIATIONS

CNTs	:	Carbon Nanotubes
CNTs-Al	:	Carbon Nanotubes impregnated with Aluminum
CNTs-Fe	:	Carbon Nanotubes impregnated with Iron
CNTs-Ag	:	Carbon Nanotubes impregnated with Silver
CNTs-Cu	:	Carbon Nanotubes impregnated with Copper
SWCNTs	:	Single Walled Carbon Nanotubes
MWCNTs	:	Multi Walled Carbon Nanotubes
AC	:	Activated Carbon
AC-Al	:	Activated Carbon impregnated with Aluminum
AC-Fe	:	Activated Carbon impregnated with Iron
AC-Ag	:	Activated Carbon impregnated with Silver
AC-Cu	:	Activated Carbon impregnated with Copper
SEM	:	Scanning Electron Microscopy
TGA	:	Thermogravimetric Analysis
EDX	:	Energy Dispersive X-ray

ABSTRACT

Full Name : **KASHIF REHAN**

Thesis Title : **REMOVAL OF AMMONIA FROM WATER USING MODIFIED NANO AND MICRO MATERIALS**

Major Field : **CHEMICAL ENGINEERING**

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Ammonia was removed from contaminated water using Carbon Nanotubes (CNTs) and Activated Carbon (AC). Impregnation was done using Fe, Al, Ag and Cu on both Carbon Nanotubes and Activated Carbon. Synthesized material was characterization using Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM) and Energy Dispersive X-rays (EDX) to confirm proper impregnation on adsorbents.

Five parameter were varied including pH, amount of dosage, contact time, shaking speed and temperature. Removal of 40% was achieved at 2g dosage with pH 10.5 at 200 RPM while silver oxide showed 10% removal at the same conditions. Temperature was also a factor of removal showing 40% removal at 70℃ as compared to 21.5% at 25℃.

Adsorption isotherm models were used for fitting the experimental data. Langmuir and Friendlich model were used where Langmuir gave better curve fitting by giving correlation factor close to unity.

Kinetic modelling with 2^{nd} order and pseudo 2^{nd} order equation were investigated. From the curve fitting graph it was concluded that pseudo 2^{nd} order kinetic model gave better fitting. As the removal percentage was low, so it can be feasible to used adsorption technique for ammonia removal by CNTs and AC as a pre-treatment method.

ABSTRACT (ARABIC)

الاسم بالكامل : **كاشف ريحان**

عنوان الأطروحة : **إزالة الأمونيا من الماء باستخدام مواد معدلة نانوية ومتناهية الصغر**

مجال التخصص : **الهندسة الكيميائية**

تاريخ الدرجة العلمية: **نوفمبر 2015**

تمت ازالة الأمونيا من المياه الملوثة باستخدام كلا من الأنابيب الكربونية المتناهية الصغر والكربون المنشط والمطعمة بأكاسيد الحديد,الالومنيوم,الفضة والنحاس. تمت المعاينة للمواد المصنعة بأستخدام تقنيات عدة مثل: تحليل حيود الأشعة السينية, والتحليل الوزني الحراري والمسح المجهري الاليكتروني والتحليل الطيفى لأشعة أكس وذلك للتأكد من أن التطعيم تم بصورة سليمة.

خلال التجارب تم تغيير خمسة عوامل وذلك لدراسة تأثيرها على نسبة الأمتزاز, هذه العوامل تشمل درجة الحموضة, كمية الجرعة للمادة الممتزة, مدة التلاس, سرعة الاهتزاز والحرارة. اظهرت الدراسة قدرة الكربون المنشط المطعم بأكسيد الامنيوم على اقتزاز% 40 من الامونيا بأستخدام 2 جم من الكربون المنشط عند درجة حموضة 10.5 وسرعة اهتزاز 200 دورة في الدقيقة من ناحية اخرى وفي مثل الظروف المذكورة اعلاه تمت ازالة% 10 فقط من الامونيا عند استخدام الكربون المنشط والمطعم بأكسيد الفضة.

أيضا تمت دراسة تأثير درجة الحرارة وتبين أنه عند رفع درجة الحرارة من 25 درجة مئوية الى 70 درجة مئوية فان نسبة امتزاز الأمونيا تزداد من 21.5% الى% 70 .

تم استخدام نموذجي لانجمير و فريندلخ لدراسة مدى ملائمتها لتمثيل النتائج, وقت أظهرت النتائج ان نموذج لانجمير اعطى نتائج أفضل.

تمت دراسة النمذجة الحركية باستخدام النموذج في الدرجة الثاني, والنموذج الشبيه بالدرجة الثانية وقد تبين من النتائج ان افضل نموذج هو النموذج الشبيه بالدرجة الثانية. حيث أن نسبة الامتزاز للامونيا كانت قليلة فاننا نرى أنه من المجدي أن يتم أستخدام هذه التقنية كمعالجة أولية.

CHAPTER 1

INTRODUCTION

1.1 General Introduction

Water plays a vital role in the life of every living creature. Fresh water being precious for its extensive use in agriculture, high technology manufacturing, and energy production, is receiving an eminent attention as a resource that require better management and sustainable use. Due to rapid development of chemical and petroleum industries, many contaminants in industrial wastewater are becoming a major issue of concern for the present day engineers.

Around 250,000 people die every year from diseases related to consumption of contaminated water (http://www.who.int). Different organic contaminants such as phenol, toluene, benzene, ethyl benzene etc. are frequently present in water resources especially in ground water. Similarly heavy metals like arsenic (As), chromium (Cr^{+6}), lead (Pb) etc. are also present in industrial wastewater which can cause fatal for human if consumed to certain extent.

One such contaminant present in water is ammonia which is a potential toxicant. It is present as organic impurity in water due organic anaerobic biological degradation of

nitrogenous compound. Many studies has proven the toxic nature of ammonia [1-4]. Due to this toxic nature of ammonia, there is a maximum allowable limit of ammonia in drinking water set by the regulatory agencies [5-6]. So ammonia concentration should be decreased to avoid its adverse effect. If the limit of ammonia exceeds 50 ppm in the atmosphere it may cause breathing problems. [Gue et al., 2004]. If contamination levels increase beyond 50-100 ppm of ammonia, it can causes irritation in eyes, throat, and nausea [7-9].

A common approach for the removal of containments from water is by ion-exchange method. Similarly, methods like thermal desalination, membranes, filtration process are also adopted in water purification processes. However, in pollution treatment technology, it is essential to consider the technology which is most cost effective. When the pollutants concentration is low or the treatment required is just to remove a single type of pollutant, then the treatment technology itself becomes extremely expensive. Hence, the requirement to find more cost effective or an economical water treatment technology becomes essential.

Adsorption is one of the techniques used to remove pollutants at a low cost with high efficiency. The target containment is adsorbed by the mass transfer on the solid adsorbent. Adsorbent materials are available in variety of forms, shapes and efficiencies. Ranging from biological adsorbent like leaf, rice husk to chemically

engineered synthesized adsorbent like zeolite are used in water treatments for the removal of containments from water.

In all those available adsorbent materials, surface area plays an important role in increasing the adsorption efficiency. In general, the larger the surface area, the larger the adsorption rate. Adsorption operation exploits the ability of certain solids preferentially to concentrate specific substance from solution onto their surface [Basava et al., 2006]. Adsorption with charred wood is employed for centuries to improve the taste of water. [Basava et al., 2006].

Micro-material like Activated Carbon (AC) and Fly Ash have proven as an alternative adsorbents for the removal of many compounds like phenol, benzene, toluene and various heavy metals [13]. Activated Carbon has a large surface area ranging from 500 to 1500 m^2/g [14]. This tremendous high surface area helps in removing undesirable elements from wastewater. This adsorption can be either physical by Wander Waal Forces or chemisorption by chemical bonding. Making use of the extraordinary properties of activated carbon, it was used in this research for the removal of ammonia.

In every aspect of life, nanotechnology is finding its way to help in solving critical problems. After the discovery of Carbon Nano-Tube (CNT) in 1991, it has gained huge appreciation among researches from different disciplines of science due to its

extraordinary mechanical and electrical properties. The most important property of these nano-structured CNTs are its high surface area. CNTs have opened new gates of solutions for many problems. Taking advantage of the properties of CNT, in this research it is used to see the effect on the removal efficiency of ammonia.

Impregnation, also known as decorating, is a practice done to further enhance the properties of certain materials. Impregnation has a similar concept as of making alloys, in which one metal is mixed in certain ratio to another metal to enhance its properties. Like Iron when mixed with chromium gives it a rust less finish.

To further enhance the properties of CNT and AC, they were impregnated with 4 different metals, namely; Fe, Al, Ag and Cu. Each of these metals have its own property, so by mixing them with CNT and AC, it gives us a wider data to compare and choose the best results of removal. Furthermore, loading of impregnated materials in different ratios (1% and 10%) was also a part of this study to analyze their effect on the removal and gives us flexibility in optimizing parameters.

1.2 Significance of the Study

An industry plays an important role in the development of a country. Every industry demands some key factors to ensure its smooth running. On one hand, where it plays an important role in the betterment of the country, at the same time on the other hand, it creates

some adverse effects on the environment. Effluent of industrial waste contains contaminants which are harmful for human and marine life.

Wastewater from industrial effluent can be a valuable source once properly treated. These effluents contain many harmful pollutants sometimes toxic which create sever effects on the environment. Most of the times, such polluted water is discharged directly into the seawater which effects the marine life. Even, people living near to those areas become the victim of these contaminants.

Ammonia, a chemical compound, is a part of many industrial applications. Problem occurs when this compound is present in industrial effluent as ammonia is considered to be toxic in nature [10-12]. The present study was conducted by applying an adsorption technique to get rid of harmful ammonia compound. In every aspect of life, nanotechnology is finding its way to help in solving critical problems.

So far, limited research has been done for the removal of ammonia by adsorption technique. In this study, not only CNT and Activated Carbon are used in raw form but they are modified as well. Impregnating CNT and Activated Carbon with Fe, Al, Ag and Cu allow us to add another step forward in adsorption.

The wastewater coming from industries are considered as polluted water. Hence, the parameters were accordingly set and concentration of ammonia was kept as high as 200 ppm and 500 ppm. This study will propose a new method for the treatment of ammonia from wastewater instead of applying traditional techniques.

1.3 Objective of the Study

The main objective of this study was to remove ammonia from wastewater. It can be summarized as follows:

1) To remove ammonia using
    i) CNT
    ii) AC
2) To prepare following metal impregnations on CNT and AC
    i) Fe
    ii) Al
    iii) Ag
    iv) Cu
3) To prepare oxides of those impregnated CNTs and ACs
4) Application of 1% and 10% of metal species impregnated on the raw CNTs and raw ACs by considering stiochmetric calculations.
5) To carry out following characterization techniques in order to confirm the impregnation
    i) TGA
    ii) FE-SEM
    iii) EDX
6) The prepare ammonia stock solution.
7) To run the experiments for following parameters and to optimize the result for best ammonia removal conditions
    i) pH
    ii) Dosage of carbon adsorbents

iii) Contact time

iv) Agitation speed

v) Temperature

8) To study the adsorption isotherms which describe the distribution of the adsorbate species between liquid and adsorbents using different isotherms such as Langmuir and Freundlich adsorption isotherms.

CHAPTER 2

LITRATURE REVIEW

2.1 Carbon Nanotubes (CNTs)

2.1.1 History of CNT

Carbon Nanotubes (CNTs) are allotropes of carbon which are rolled up tubular shells of graphene sheets as shown in Figure 2.1. These graphene sheets have structures similar to benzene type hexagonal rings of carbon atoms which are made of C atoms placed at the corners of hexagons forming the lattice.

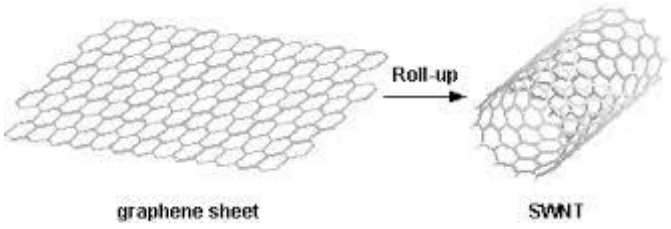

Figure 2.1: CNT from graphene roll up

These CNTs can be studied under applied quantum chemistry, especially, orbital hybridization. The main bond forces are in the form of sp^2 which are quite similar to graphite bonding. sp^2 bonds are stronger than sp^3 bonds, which provides CNT its unique strength. Moreover, Vander Waal forces are the dominating forces which holds the nanotubes together [16].

The extraordinary properties of nanotubes are based on structural arrangements. Their electrical conductivity is the result of hexagonal rings along the tubular surface which gives them metallic or semi conducting behavior. Keeping in mind the exceptional properties of carbon nanotubes including large geometric aspect ratios and nano-cavities, CNTs have made its unique value in nanotechnology applications including water treatment.

Though CNTs have shown a great application potential, it has some disadvantages too. One of which is its lackness of solubility in solvents which makes a great limitation for its use in industrial application [17]. Alternatively, by sonication and through chemical reactions and adding functional groups, it can be made soluble for inorganic and organic solutions.

2.1.2 Types of CNTs

Carbon Nanotubes are broadly divided into 2 categories.

1. Single Walled Carbon Nanotubes (SWCNTs)
2. Multi Walled Carbon Nanotubes (MWCNTs)

As reported by Wang [15], SWCNTs has an approximate diameter of 1 nanometer with a tube length from few micrometer to 18 centimeter in length. To visualize, we can consider SWCNT as rolled up tubular shells of graphene sheets.

These graphene sheets can be rolled up in 3 different forms [18].

- Zig-Zag SWCNT
- Chiral SWCNT
- Arm Chair SWCNT

$$R = na_1 + ma_2$$

Where a_1 and a_2 are unit vectors and R donated resultant vector.

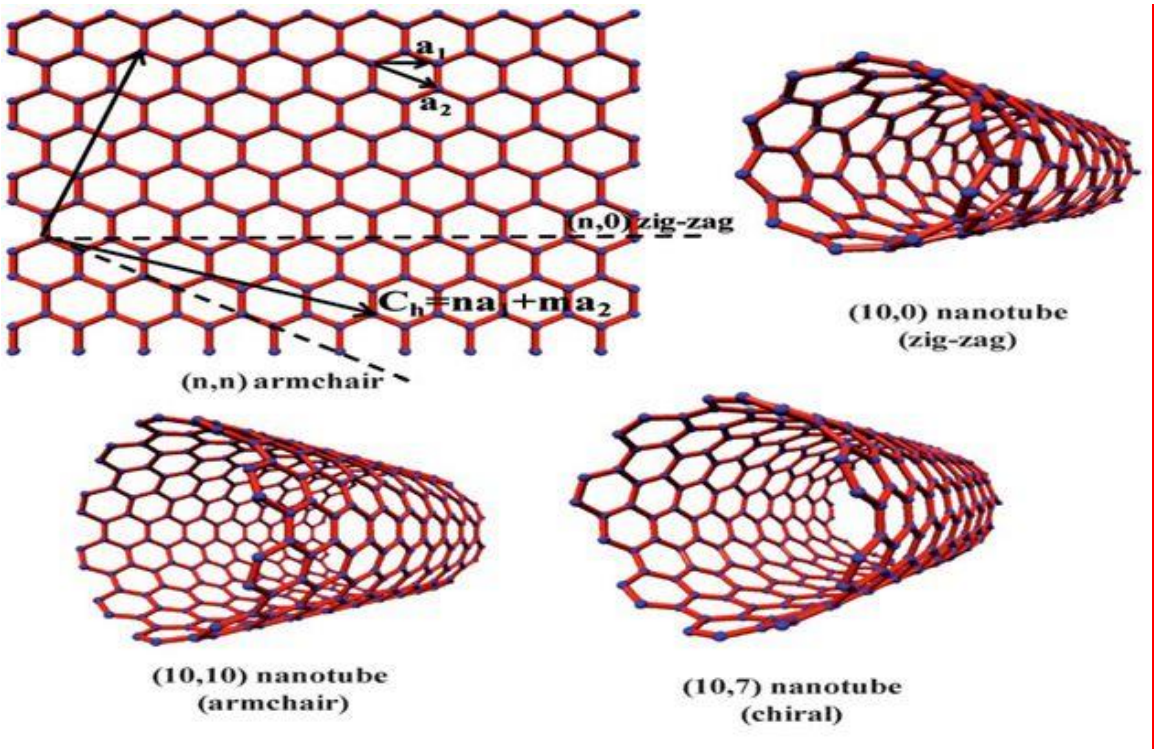

Figure 2.2: Structure of SWCNT and Chiral factor

Indicators (n, m) are called chiral vectors which demonstrate the shape and geometry of rolling of sheets. If m=0 then it gives zig-zag pattern whereas arm chair pattern is obtained when n=m [19]

Multi Walled CNTs

If one graphene sheet is rolled up on to another graphene sheet in such a way that they have concentric assembly then these SWCNTs are called MWCNTs as shown in Figure 2.3. Due to modification in structure, their properties differ from each other a lot as well [20].

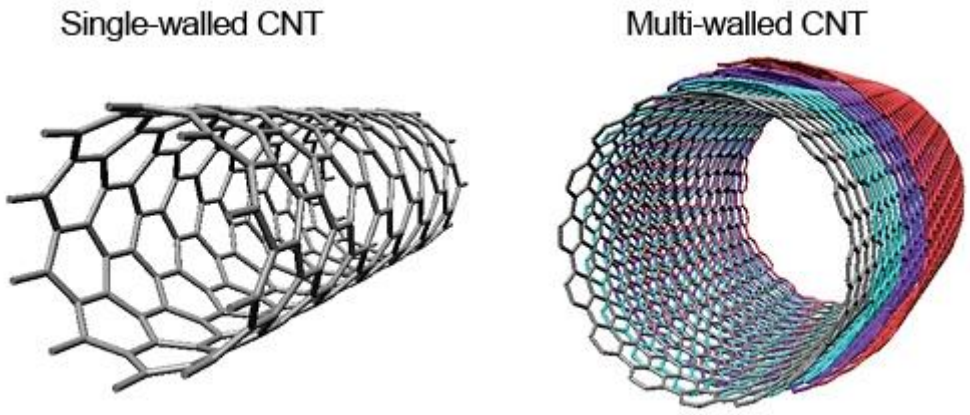

Figure 2.3: Structure of SWCNT and MWCNT

2.1.3 Properties of CNTs

1. Electrical Properties

Electrical properties of CNT are strongly dependent on its structural type. According to classification of geometry as zig-zag, chiral or arm chair, CNTs can be metallic or semi

conducting. The conductive properties of CNTs can be way better than copper wire [21]. The chiral factor [n, m] plays an important role in describing the metallic or semiconductor behavior. If the difference between n and m for specific values of [n, m] is a multiple of 3 then it is a metallic nanotube. If it lack this property then it exhibits a semiconductor property. All arm chair [n=m] are metallic in nature [21].

2. Thermal Properties

Around 6600 W/m.K of thermal conductivity at room temperature for an isolated nanotube was reported by Berber *et al.* Along the axis, CNT shows very high thermal conductivity because of vibrations of carbon atoms and its free movements along the tubes.

3. Mechanical Properties

Due to strong bond between the atoms of CNTs, it is considered to be the stiffest material on earth. Because of the flexible nature of CNT, it can be elongated, twisted, flattened or bent into shapes before fracturing. The elastic module of CNT is 1 TPa which is approximately 10-100 times higher than steel at a fraction of weight [25]. It has been shown that even at high strain amplitude up to half a million cycle, MWCNT shows no fatigue failure.

Table 2.1: Mechanical properties of carbon nanotubes (Yamabe, 1995)

Material	Young's modulus (GPa)	Tensile strength (GPa)	Density (g/cm^3)
SWCNT	1054	150	1.9
MWCNT	1200	150	2.6
Steel	208	0.4	7.8
Epoxy	3.5	0.005	1.25
Wood	16	0.008	0.6

4. Chemical Reactivity

One of the disadvantages of CNT is its insoluble nature in all organic solvents, which limits its usage in industrial applications. However, while undergoing chemical reactions, CNTs can be made soluble in inorganic, organic and biological solutions

3 different classes of chemistry of CNTs were mentioned by *Dimitrios* [26]

1. Non-Covalent adsorption of various functional molecules.
2. Reaction on π conjugate skeleton of CNT by covalent attachment.
3. Inner empty cavity filling.

2.1.4 Production of CNT

There are many techniques available for the production of CNTs. However, some of the widely used are as follows:

1. Laser Ablation Method

At temperature 1200℃ in an oven, Richard Smalley reported that CNTs can be synthesized using laser beams by vaporizing graphite target [27]. The evaporated material condenses on the surface of reactor to produce MWCNTs. Similar method can be used for the synthesis of SWCNTs with the use of Co, Ni and Fe as catalyst [28]. There are two types of laser methods used currently; continuous and pulse. Light intensity is the main difference between the two.

2. Arc Discharge Method

Helium gas or other neutral atmosphere at low pressure are used in Arc Discharge method to synthesis CNT [29]. Arc Discharge Method is the method by which CNT was first discovered in 1991 as shown in the Schematic Diagram in Figure 2.4 and till today it is the simplest and easiest method to produce CNTs on large scale. In this method, low pressure inert atmosphere is used to ignite arc between two graphite electrodes [30]. After it cools and condenses, some of the carbon products are deposited on cathode in the form of film.

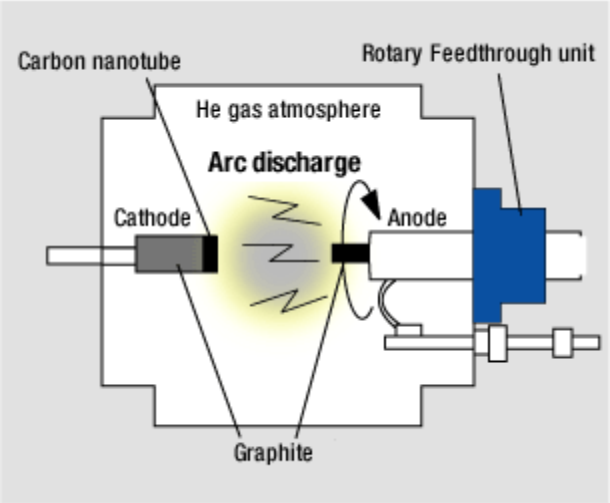

Figure 2.4: Schematic Diagram of an arc-Discharge system

3. Chemical Vapor Deposition (CVD)

In CVD, at first, the catalyst is prepared and then the actual synthesis of CNTs take place. It is the most common method used for production of CNTs on industrial scale. It gives enough flexibility and control to produce high purity CNTs by varying parameters.

At 500℃ to 1000℃, carbon source in gas phase is passed over energy source which cracks the molecules into atomic carbon. CNTs are produced when these active carbon atom penetrate into substrate which are then heated and coated with catalyst. (Fig 2.5)

The fundamental procedure involves dissociation of hydrocarbon molecules which are catalyzed and precipitated. Tubular carbon solid in sp^2 structure are synthesized in this process.

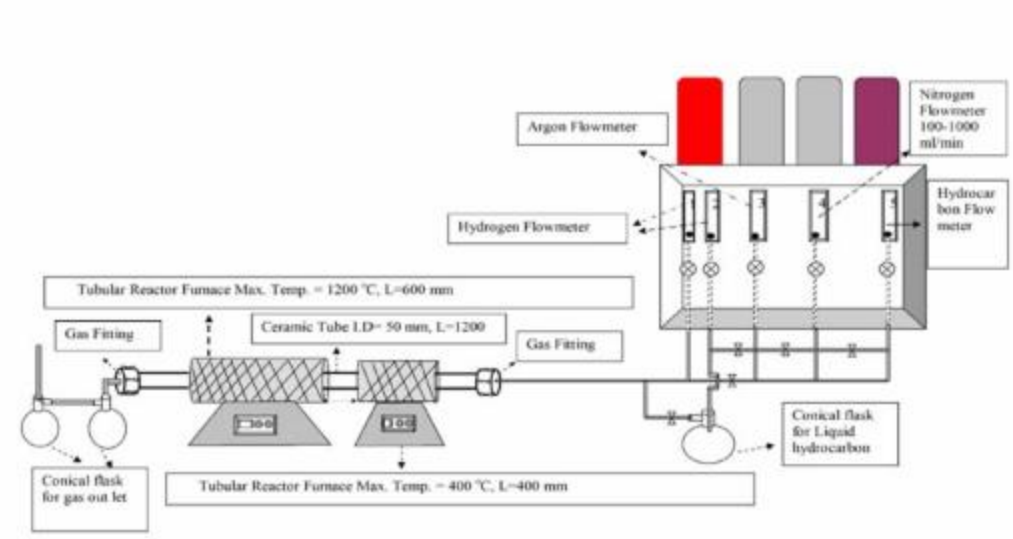

Figure 2.5: A schematic diagram of a double-stage CVD apparatus (Muataz et al., 2005)

2.2 Activated Carbon (AC)

2.2.1 What is Activated Carbon (AC)

Activated carbon has an amorphous and highly porous structure which belongs to carbon family. It is also referred to as activated charcoal. Due to its high micro porosity, it has gained special attention by the researchers in different disciplines of science. 1 gram of activated carbon has surface area of more than 500 m^2 [31].

Activated carbon has been used by ancient Egyptians for medical purposes [32]. Historically, it has been used for purification mainly for sour taste and odor [33]. Many low

cost or waste materials are used to produce activated carbon. Some of them include coconut shell, wood, refineries coke, rice husk and some organic materials.

Application of adsorption procedure require high surface area and surface reactivity. Activated carbon has both of these features because of its micro porous structure.

2.2.2 Types of Activated Carbon

On the basis of activation process, activated carbon are classified into different groups. Some of the major classification based on their physical characteristics are as follows [35]:

1. Powdered Activated Carbon (PAC)

PAC is finer material. It is either powdered or fine granular with approximate size of 1mm having average diameter of 0.15 to 0.25 mm [34]

2. Extruded Activated Carbon (EAC)

Diameter range from 0.8 to 130 mm in cylindrical shape and extrude geometric are the feature of extrudate activated carbon. Due to their low pressure drop, they are used in gas phase applications.

3. Granular Activated Carbon (GAC)

GAC has relatively large particle size as compared to PAC which makes its surface relatively smaller. Mostly, they are used for adsorption of gases because of their rapid diffusive nature. Deodorization and water treatment are its main applications. Different granular size are made for various applications like 8x20, 20x40 etc.

4. Polymer Coated Carbon

Bio compatible polymer are coated to give smooth finishing and permeable coat. Its main application is in medical treatments like detoxifying blood.

5. Impregnated Activated Carbon

Decoration of some inorganic elements like Al, Fe, Ag and Cu enhances the properties of activated carbon. These impregnation techniques vary from application to application and is also a major function of element used.

6. Beats Activated Carbon (BAC)

It has a spherical shape which is a preferred geometry for fluidized bed. Its diameter ranges from 0.35 to 0.8 mm. It also exhibits properties of being high mechanical strength, low dust content and low pressure drop.

2.2.3 Properties of Activated Carbon

On industrial scale, there is hardly any industry where activated carbon is not a part of process. From deodoring to filtering, Activated carbon due to its high surface area, it enjoys a unique value in adsorption materials.

Activated Carbons are similar to graphene sheets in which π orbital in carbon rings plays an important role and gives flexibility to modify the surface. Due to these properties, surface of activated carbon can be modified / impregnated with other materials to enhance

its adsorption properties. Activation process also plays a vital role in defining the pore size and hence the adsorption behavior.

2.2.4 Production of Activated Carbon

Activated Carbon is an ancient adsorbent and its production is well known. Many raw materials can be used in production of Activated Carbon, like coconut shell, wood, carbon black, rice rusk etc. Nowadays Activated Carbon is produced mainly by two different processes.

1. Steam Activation

All raw materials can be involved in this steam activation method for AC production. Temperature of about 500℃ to 600℃ is maintained to remove all volatile compounds from raw material. This step is called carbonization. Then, activation with steam at 800℃ to 1800℃ is maintained to develop the desired porosity and surface area. Since this activation step is exothermic, so its energy can be utilized.

$$C + H_2O\ (steam) \rightarrow CO + H_2$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O\ (steam)$$

$$C + O_2 \rightarrow CO_2$$

2. Chemical Activation

Before the carbonization step, Activated Carbon is pretreated by adding some inorganic additive and activation agent like phosphoric acid. These regents and raw materials are heated together at 600℃. This process improves the microporous structure of activated carbon.

2.3 Ammonia and its toxicity

Ammonia is a colorless, pungent and corrosive gas by its nature. It is found in atmosphere as nitrogen compound excessively after nitrogen and nitrous oxide [36]. During recent years, environmental issues related to ammonia nitrogen polluted water has become a serious problem. The main source of ammonia nitrogen is enzymatic breakdown of urea, proteins and other nitrogen containing materials.

Among many sources of ammonia nitrogen pollution, one major source is the wastewater effluent from industries like steel, refining, fertilizers, feed production etc. The guidelines regarding ammonia release into the receiving water are different in different parts of the world. According to Environment Protection Agency (EPA), the allowable value of ammonia nitrogen is 0.02 ppm [37]. The council of European Communities based their guideline on 0.05 ppm (mg/l N-NH_3) with maximum allowable value as 0.5ppm [38].

Difference between NH_4^+ and NH_3

The ionized ammonia (NH_4^+) and unionized ammonia (NH_3) are interrelated through chemical equilibrium.

$$NH_4^+ - OH \leftrightarrow NH_3.H_2O \leftrightarrow NH_3 + H_2O$$

The sum of NH_4^+ and NH_3 concentration are referred to as Total Ammonia Nitrogen (TAN). Their relative concentration is pH dependent. With the increase in water pH, concentration of NH_3 also increases with the relative decrease in NH_4^+. In regards to toxicity level, unionized ammonia (NH_3-N) is more toxic to aquatic animals, particularly to fish however ionized ammonia nitrogen (NH_4^+-N) is apparently less toxic.

2.4 Conventional Methods

Chemical industries excessively use ammonia as a cleaning and beaching agent, in the production of fertilizers, plastic etc. As a result, they produce large quantities of wastewater containing ammonia. Some of the conventional method used in last decades for ammonia removal and some new techniques are discussed below:

2.4.1 Ion Exchange Method

Ion exchange method has been used in various field in recent years. Due to high treatment capacity, high removal efficiency, fast kinetics and low cost of ion exchange procedure, it is used for ammonia removal from wastewater [39]. Among many ion

exchange compounds, zeolite has its unique importance because of its highly porous and different cavity structure with negative charge lattices [40].

The general formula of zeolite is

$$(M_x^+, M_x^{2+})\left(Al_{(x+2y)}Si_{in-(x+2y).}O_{2n}\right).mH_2O$$

Where M^+ and M^{2+} are monovalent and divalent cations such as Na^+, K^+ and Ca^{2+}, Mg^{2+} respectively. Al^{3+} and Si^{4+} are structural cations which makeup the framework of structure with O [41]

Zeolite and certain natural zeolites like; Clinoptilolie has been found effective in controlling ammonical nitrogen. The use of traditional ion exchange resins in removing ammonia from feed water can be obtained by normal cation exchange softeners.

2.4.2 Biosorption

Biosorption has confirmed some promising results in ammonia removal in recent years. Generally, biosorbents are inexpensive and highly effective in reducing the ions. Diluted ammonia wastewater containments can also be well treated by biosorption process.

Three main sources of biosorbents are as follows [42]

1. Non-living biomass such as crab shells, shrimp etc.
2. Algal biomass
3. Microbial biomass (bacteria, fungi etc.)

Some of the biological techniques used in recent years for ammonia treatment includes; wet air oxidation (WAO) [43], Ozonation [44], intermediate biofilters IBF [45], nitrification and denitrification [46].

2.4.3 Liqui-Cel® membrane

Numerous conventional ways used to remove ammonia, produce secondary waste which can cause a whole list of other problems. In the last few years, membranes have played an important role in removing many toxic compounds from water. Membrane contractors offer a superior solution for stripping ammonia because of their large surface area. Liqui-Cell® membrane contactors are used for extraction process. Some of the advantages are as follows:

- The process is durable and reliable
- It is cost effective
- Some commercial valuable material can be extracted.

CHAPTER 3

METHODOLOGY

3.1 Characterization of Adsorbent

To confirm the morphology (Diameter and length) of the adsorbents, different characterizing technique were used. The Field Emission Scanning Electron Microscopy (FE-SEM) was used to characterize the length and diameter of CNT and AC. Thermogravimetric Analysis (TGA) and Derivative Thermogravimetric (DTG) curves were obtained for all adsorbents at heating rate of 10℃ / min which ensures the presence of impregnated material in addition to raw CNT and AC. Energy Dispersive X-Ray (EDX) technique clearly indicates the presence of specific impregnated material and its percentage loading on the adsorbent.

3.2 Preparation of Ammonia Stock Solution

Stock solution with concentration of 300 ppm was prepared from 30% purity ammonia solution commercially available. According to relation, 1% = 10,000 ppm, the commercially purchased solution was 300,000 ppm. Then, it was diluted to required concentration (300 ppm and 500 ppm) by using the relation

$$M_1V_1 = M_2V_2$$

Where, the subscript "1" refers to concentrated solutions and the subscript "2" refers to diluted solutions.

For preparation of 300 ppm stock solution, 2 ml of 30% ammonia solution was pipetted to 2000 ml flask with constant stirring. The pH of the stock solution was adjusted by using 1.0M HCL for acidic media and 1.0M NaOH for basic media.

3.3 Ammonia Electrode Calibration

The Orion 95-10 Ammonia Electrode was used for the accurate measurement of dissolved ammonia in aqueous solution.

The summary of steps involved in calibrating the electrode are as follows:

1. It was made sure that all samples, standards and electrode was at same temperature.
2. 3.819 g of NH_4Cl salt was added in 1000 ml flask and filled with deionized water up to the mark with constant stirring giving us 1000 ppm of solution
3. After that stepwise dilution was done to prepare 100 ppm, 10 ppm, 1 ppm and 0.1 ppm making use of relation $M_1V_1 = M_2V_2$
4. The electrode was connected to meter with millivolt readout
5. Starting from lowest concentration (0.1 ppm), 100 ml was transferred to 150 ml beaker. Then the electrode was dipped and 1-2 ml of 10 N NaOH was added to the solution with constant stirring.
6. The meter reading was recorded when stabilized.
7. Similarly millivolt reading was recorded for 100 ppm, 10 ppm and 1 ppm.

8. From the data, semi log plot was constructed having concentration on log x-axis and mV on y-axis.
9. It gives a curve similar to the one shown in Figure 3.1. Making use of the curve, unknown concentration of ammonia can be calculated. [Electrode manual]
10. Conversion factor among the concentration of ammonia is shown in Table 3.1

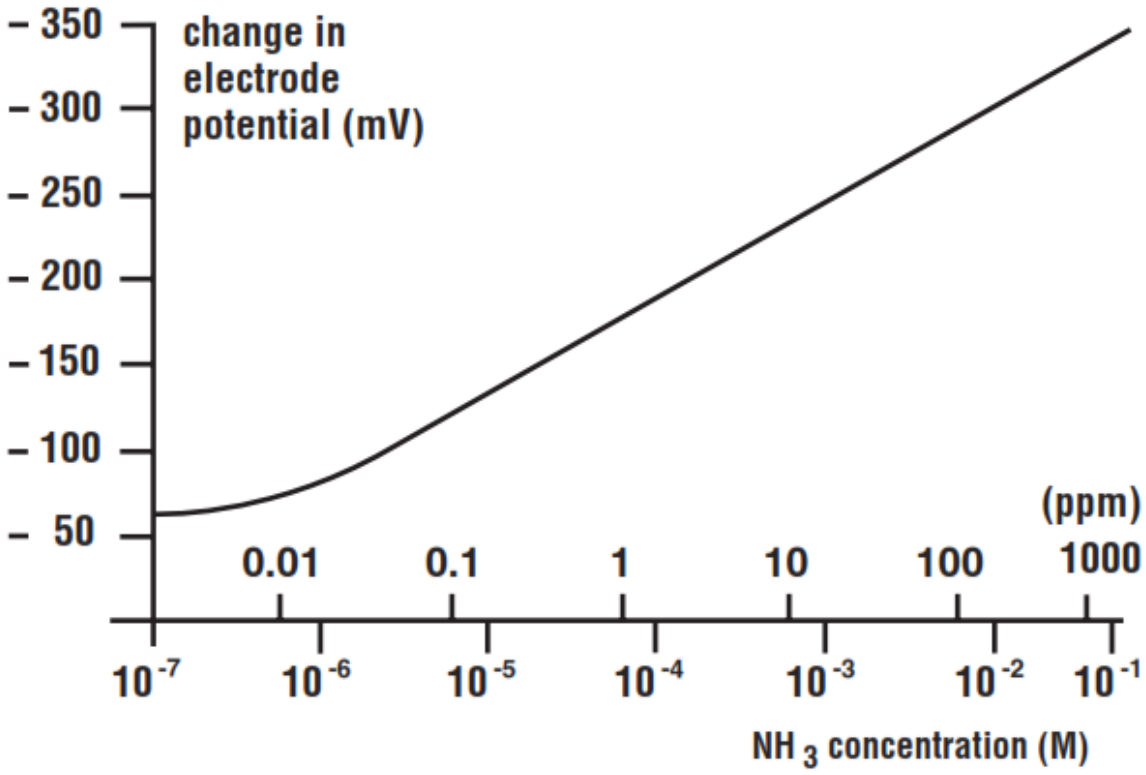

Fig 3.1: Standard Calibration Curve [Electrode Manual]

Table 3.1: Conversion factors [Electrode Manual]

Moles/Liter	ppm as N	ppm as NH_3
10^{-4}	1.40	1.70
10^{-3}	14.0	17.0
10^{-2}	140	170
10^{-1}	1400	1700

3.4 Batch Adsorption Mode Experiment

Each experiment was conducted in a volumetric flask of 100 ml volume with cap. As ammonia is a volatile compound, it should be covered to avoid vaporization. The experiments were conducted at room temperature where different parameters (pH, contact time, agitation speed, dosage and temperature) were varied to see the adsorption effect.

Whattman no. 1 filter paper was used to filter the samples in order to determine the final concentration and hence percentage removal. The amount of ammonia adsorbed on the MWCNTs and AC was determined by the difference of the initial concentration (C_i) and the final concentration (C_f). The percentage removed of NH_3-N from the solution was calculated using the following relationship:

$$\% \, Removal = \frac{C_i - C_f}{C_i} \times 100$$

The metal adsorption capacity (Q_e) was calculated by the following equation:

$$Adsorption\ capacity\ Q_e\ \left(\frac{mg}{g}\right) = \frac{C_i - C_f}{M_s} \times V$$

Where:

V = volume of the solution (L)

M_s = weight of adsorbent (g)

C_i = Initial concentration (ppm)

C_f = Final concentration (ppm)

3.4.1 Effect of pH

The effect of initial pH of solution on adsorption capacity was studied by varying the pH value from 9-11 while keeping all other parameters fixed. The volumetric flask containing the solution was shaken at different pH levels for maximum of 4 hours. 1.0 M NaOH for increasing the pH to basic media and 1.0M HCl for decreasing the pH to acidic media were used to adjust the desired value of pH

3.4.2 Effect of Shaking Speed

Speed of agitation was varied from 100 – 250 RPM to see the effect on adsorption capacity of ammonia by both CNT and AC. Agitation speed study was done after optimizing the pH value. Mechanical shaker with digital controller was used to provide accurate reading. The final concentration was analyzed by the ammonia electrode after filtering the solution by Whatman No.1 filter paper.

3.4.3 Effect of Contact Time

The effect of contact time between adsorbent and adsorbate was studied by allowing the solution to shake with optimal agitation speed on different time intervals. Experiments were conducted at various time intervals ranging from 30 mins to 1, 2, 4, 12 and 24 hours. After each experiment, the sample was filtered and ammonia concentration was analyzed to investigate the effect of contact time.

3.4.4 Effect of Adsorbent Dosage

After optimizing pH value, the next parameter to be varied was to investigate the effect of adsorbent dosage on the removal efficiency of ammonia. All the adsorbent (CNT, AC and impregnated CNT and AC) were added in different capacity ranging from 0.05, 0.1, 0.5, 1, 1.5, 2 g in volume of 100 ml. The resultant concentration was analyzed by ammonia electrode after filtering each sample by Whatman No. 1 filter paper

3.4.5 Effect of Temperature

Temperature effect was also one of the parameter to observe. With the variation of temperature, the motion of the molecules are also changed and ammonia molecules has

more chances of interaction with the adsorbent material. To investigate this behavior, the study was conducted at 3 different temperatures (25℃, 50℃ and 70℃) keeping other parameters constant to observe the temperature effect solely.

3.5 Experimental Design

The experimental model for ammonia removal research work is summarized as follows:

Table 3.2: Experimental parameters and its variation

pH	Adsorbent Dosage (g)	Agitation Speed (RPM)	Contact Time (hr)	Temperature (℃)
9	0.05	100	30 (min)	25
10	0.1	150	1	50
11	0.5	200	2	70
	1	250	4	
	1.5		24	
	2			

3.6 Impregnation of Ions on the Adsorbents

Impregnation is a practice done to enhance the properties of a material. In this study, four metal oxides were impregnated on carbon nanotubes and activated carbon having ratio of 1% and 10%. Those four metal oxides are iron oxide, aluminum oxide, silver oxide and copper oxide.

- Iron (Fe) oxide was prepared from Ferric nitrate [$Fe(NO_3)_3.9H_20$)]
- Aluminum (Al) oxide was prepared from aluminum nitride [$Al(NO_3)_3.9H_2O$]
- Silver (Ag) oxide was prepared from silver nitrate [$AgNO_3$]
- Copper (Cu) oxide was prepared from copper (III) nitrate [$Cu(NO_3)_2.3H_2O$]

Summary of the preparation procedure of impregnated material are as follows:

1. To prepare 20 g of impregnated materials, stiochmetric amount of chemical salts (Ferric nitrate, aluminum nitride, silver nitrate and copper (III) nitrate) was measured by using Mettler Toledo balance.
2. Each of the samples were mixed in 200 ml ethanol (purity 98%) in a beaker until it was completely dissolved.
3. CNT and AC were measured as 19.8 g for 1% impregnation and 18 g for 10% impregnation and then added to the beaker containing ethanol and salts.
4. The beaker was sonicated for 30 min at amplitude 40 for proper dispersion of impregnation materials on CNT and AC.
5. After sonication, the mixture was kept in oven for 24 hour at 70℃ to evaporate ethanol. The mixture was kept in furnace for 3 hours at 350℃ for calcination.
6. Finally the materials were characterized to ensure proper impregnation of materials on CNT and AC.

3.7 Adsorption Isotherm Models

Distribution of adsorbate species among liquid and adsorbent are best described by adsorption isotherms. These are the mathematical models having set of assumptions related to the possibility of interaction between the adsorbate species. Among many isotherm models, Langmuir and Frendlich are common isotherms for fitting the experimental data.

The Langmuir model assume that the adsorption is localized in a monolayer and there are no interaction between adsorbate molecules. The Frendlich isotherm model however assumes that different sites with several adsorption energies are involved. It is an empirical relationship where adsorption of solute from liquid to solid is described.

The Langmuir isotherm model is usually considered the best known of all the isotherms and is defined as

$$Q_e = \frac{Q_m(KC_e)}{(1+KC_e)} \quad (1)$$

Where;

Q_e *= the adsorption density at the equilibrium solute concentration C_e (mg of adsorbate per g of adsorbent)*

C_e *= the equilibrium adsorbate concentration in solution (mg/l)*

Q_m *= the maximum adsorption capacity corresponding to complete monolayer coverage (mg of solute adsorbed per g of adsorbent)*

K *= the Langmuir constant related to energy of adsorption (l of adsorbent per mg of adsorbate)*

The above equation can be rearranged to the following linear form:

$$\frac{C_e}{Q_e} = \frac{\mathbf{1}}{Q_m K} + \frac{C_e}{Q_m} \quad (2)$$

Linearization of experimental data can be done by equation (2) where value of $\frac{C_e}{Q_e}$ is plotted against C_e to give a straight line. Langmuir constant (Q_m and K) can be evaluated from slope and intercept respectively.

Alternatively, Frendlich isotherm model can be used if Langmuir isotherm doesn't give good data fitting.

Freundlich model is expressed as:

$$Q_e = K_f (C_e)^{1/n} \quad (3)$$

Where:

Qe *= is the adsorption density (mg of adsorbate per g of adsorbent)*

Ce *= is the concentration of adsorbate in solution (mg/l)*

$\boldsymbol{K_f}$ *and* ***n*** *are the empirical constants dependent on several environmental factors and* ***n*** *is greater than one.*

This equation is conveniently used in the linear form by taking the logarithm of both sides as:

$$\ln Q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e \quad (4)$$

A plot of ln [C_e] against ln [Q_e] yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The constants can be determined from the slope and the intercept.

3.8 Kinetic Modeling

Residence time of the adsorbate between the solid liquid interface and removal rate of the adsorbate, can be best described by the sorption kinetics. In order to evaluate the mechanism of the sorption of ammonia on all carbon based adsorbents, following relations were applied.

1. First order Equation:

$$\ln \frac{Q_e - Q_t}{Q_e} = -\frac{K_L t}{2.303} \quad (5)$$

The calculated quantities of $\ln(Q_e - Q_t)$ will be plotted versus time (t)

2. The pseudo – second order rate equation:

$$\frac{t}{Q_t} = \frac{1}{2K_s Q_e^2} + \frac{t}{Q_s} \quad (6)$$

The calculated quantities $\frac{t}{Q_t}$ will be plotted versus time (t)

3. The second order rate equation:

$$\frac{1}{Q_e - Q_t} = \frac{1}{Q_e} + K_2 t \quad (7)$$

The calculated quantity $\left(\frac{1}{Q_e - Q_t}\right)$ will be plotted versus time (t)

Where:

Q_e = sorption capacity at equilibrium

Q_t = sorption capacity at time (mg/g)

K_L = the Lagergren rate constant of adsorption (1/min)

K_2 = rate constant of the pseudo second-order sorption ($g.mg^{-1}.min^{-1}$)

t = time (min)

From the best fit for the linear equations, the representative kinetics model for each adsorbent was determined.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Adsorbents Characterization

4.1.1 Field Emission Scanning Electron Microscopy (FE-SEM)

This is a technique used to investigate molecular surface structure. The samples are kept on beads in small quantity and then coated with 7 mm thick layer of platinum to increase the conductivity of surface.

Carbon Nanotube diameter ranges from 20-40 nm with an average diameter of 24 nm having few microns in length. In comparison to CNTs, activated carbon showed an average diameter ranges between 600-1000 microns. Presence of crystals on the CNT and AC indicated the presence of impregnated material on them. [Figure 4.1]

It can be seen from the following figures that there is a presence of some trace metals present on the surface of carbon materials. These traces from the SEM images confirms the impregnation of other species on the CNT and AC surface and modification of surface morphology.

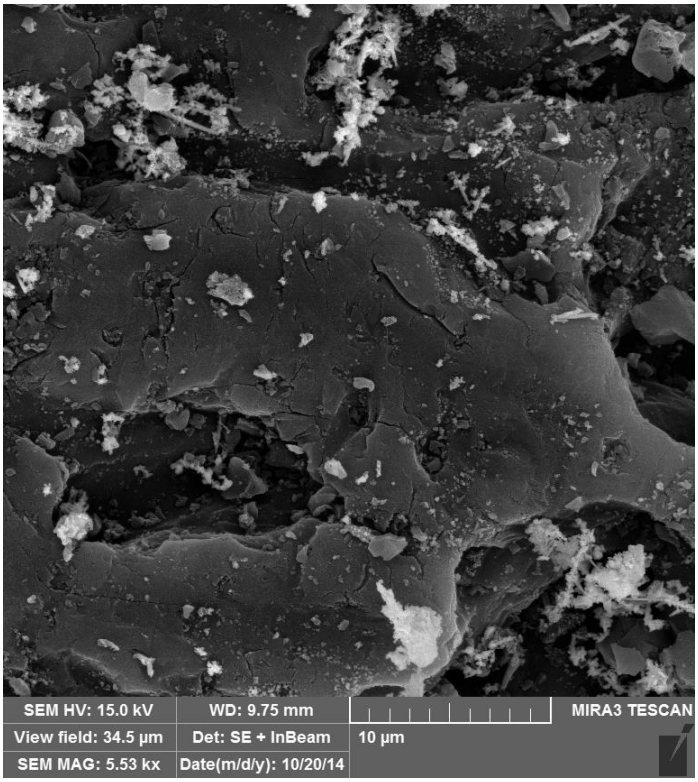

Figure 4.1: AC + 1% Ag

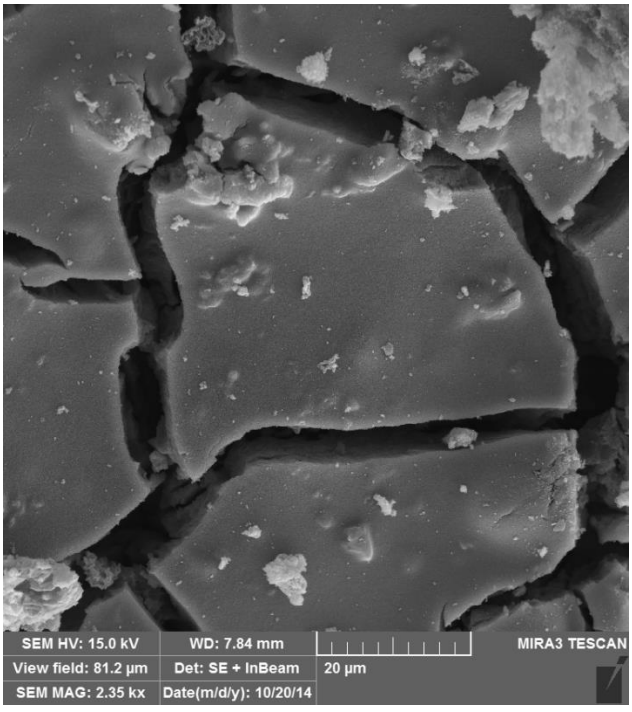

Figure 4.2: AC + 10% Fe

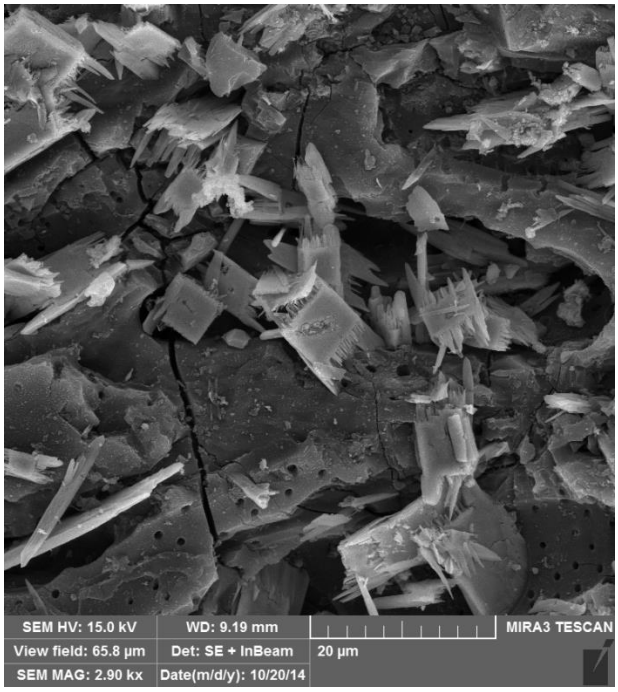

Figure 4.3: AC + 10% Cu

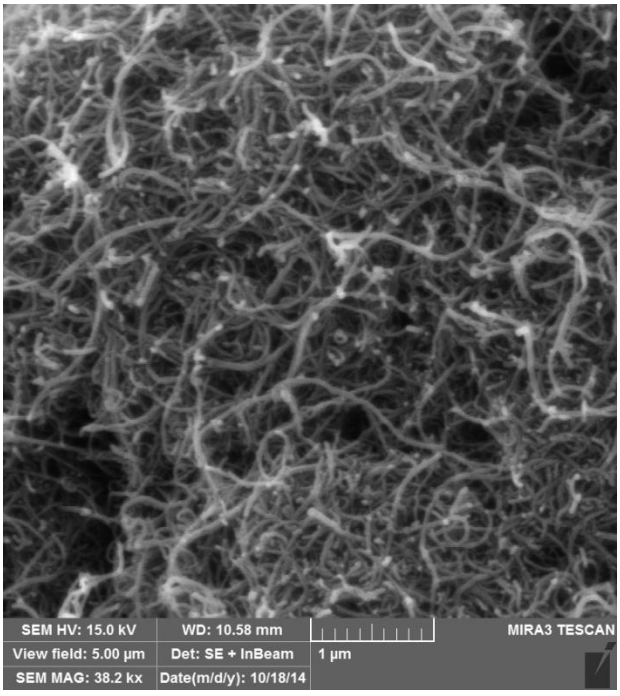

Figure 4.4: Pure CNT

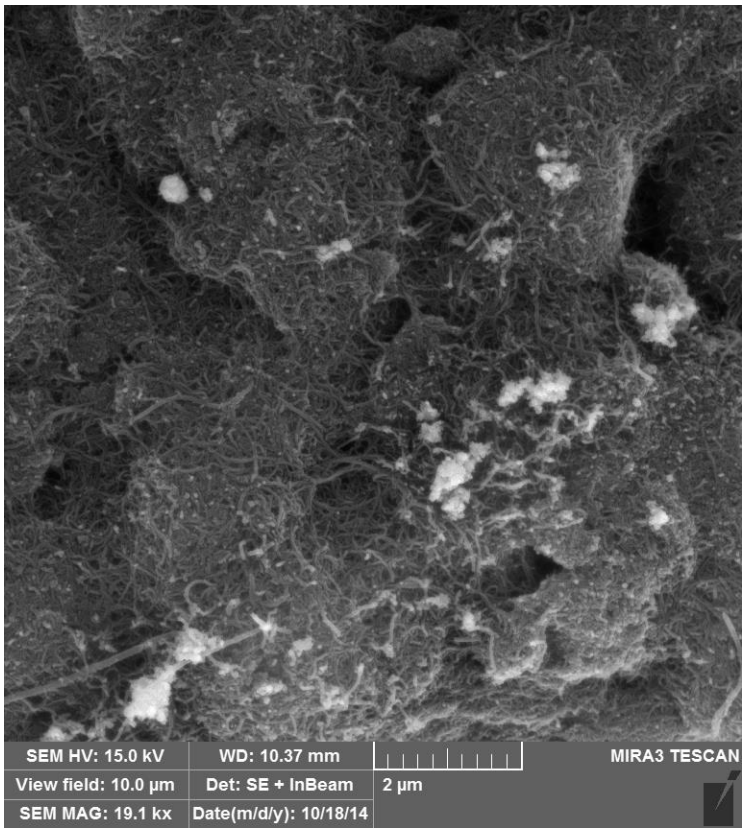

Figure 4.5: CNT + 10% Ag

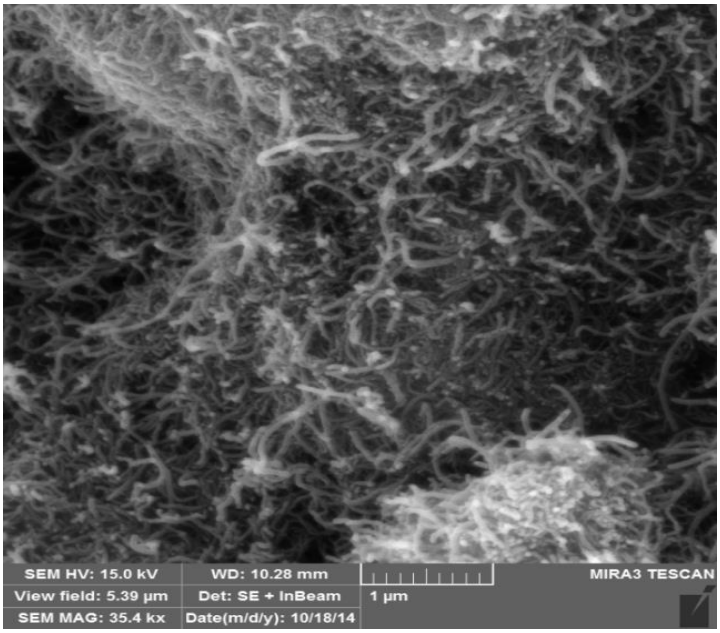

Figure 4.6: CNT + 10% Al

4.1.2 Energy Dispersive X-Ray Spectroscopy (EDX)

EDX, an analytical technique which indicates the presence of different elements on the sample. With respect to impregnation, this characterization technique plays an important role in confirming the proper impregnation of specific metals. [Figure 4.7]

With proper analysis of the sample, EDX can also be used to identify the weight percent loading of metals on adsorbents. Peaks other than carbon elements shown in the below images from the EDX results shows the exact element present on the material (CNT and AC) surface. In some results like in [Fig 4.9], traces of other metals like Si, was seen which were in very minute quantity from the production source.

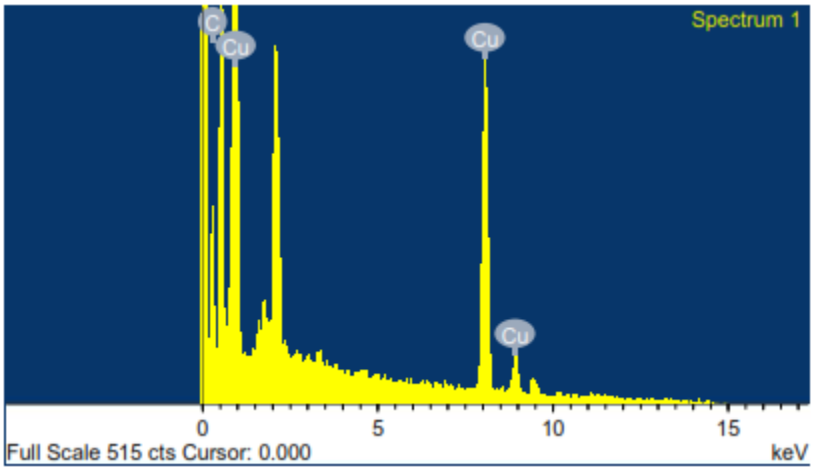

Figure 4.7: AC + 1% Cu

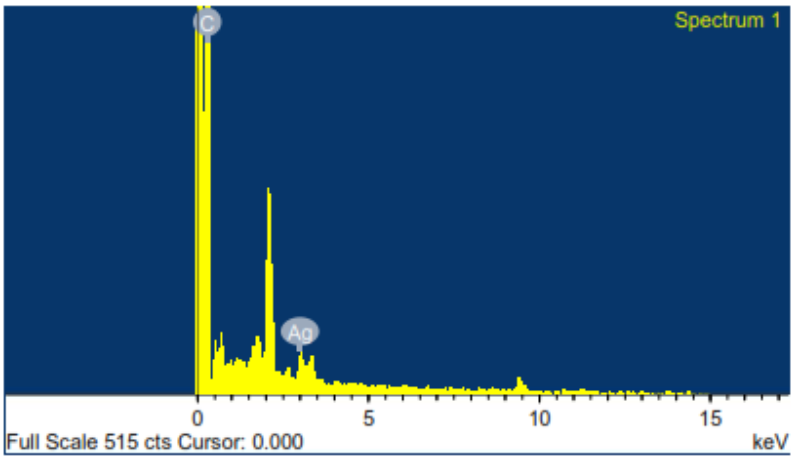

Figure 4.8: AC + 10% Ag

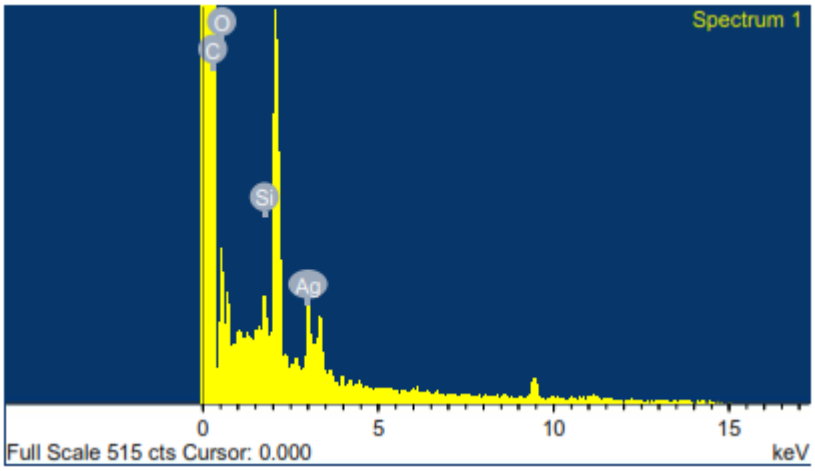

Figure 4.9: CNT + 1% Ag

4.1.3 Thermogravimetric Analysis (TGA)

TGA and Derivative TGA (DTGA) is a thermal analysis technique which confirms surface morphology by increasing temperature at constant rate. In my TGA analysis, all samples were heated at constant rate of 10℃/min in the presence of air upto 900℃. CNT and AC

were oxidized, however, some residual were left in the pan which indicated the presence of trace metal like reddish ash in case of Fe impregnation.

CNT decomposition is a single stage decomposition reaction. It can be seen in the Figure. 4.10, that for 10% loading, the initial degradation started at approximately 450℃ followed by a sharp decline in graph indicating a rapid weight loss from 450℃ to 530℃. Finally, when the temperature reached 900℃, the weight loss is close to 20%. This result is then compared to pure CNT graph. 10% more ash left in the pan confirm the presence of Fe impregnation. Similarly 1% metal loading is also shown for comparison.

Similar trend was seen in Figure 4.11, where pure CNT is compared with 1% and 10% loading of Al material. Higher value in 10% loading at the flat end shows that some Al was presence in the pan which confirm the presence of impregnated material.

As CNT and AC, both belong to same carbon family so the trend in TGA result for both of them were similar. AC has also shown a gradual degradation in the weight% until it reaches 450℃, where sharp loss in weight was noticed till 530℃. When comparing pure AC with 1% and 10% loading of different materials, 10% loading was always higher in weight% at the end which more percentage of material is left in the pan confirming the presence of impregnation.

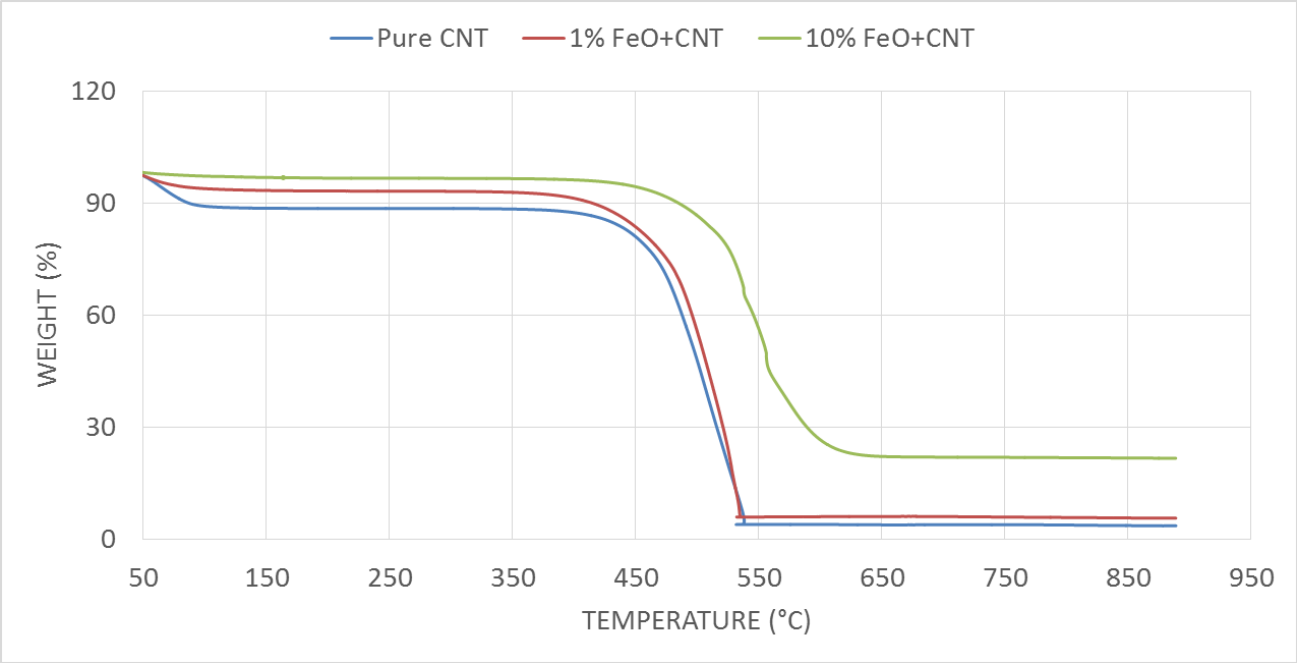

Figure 4.10: CNT + FeO

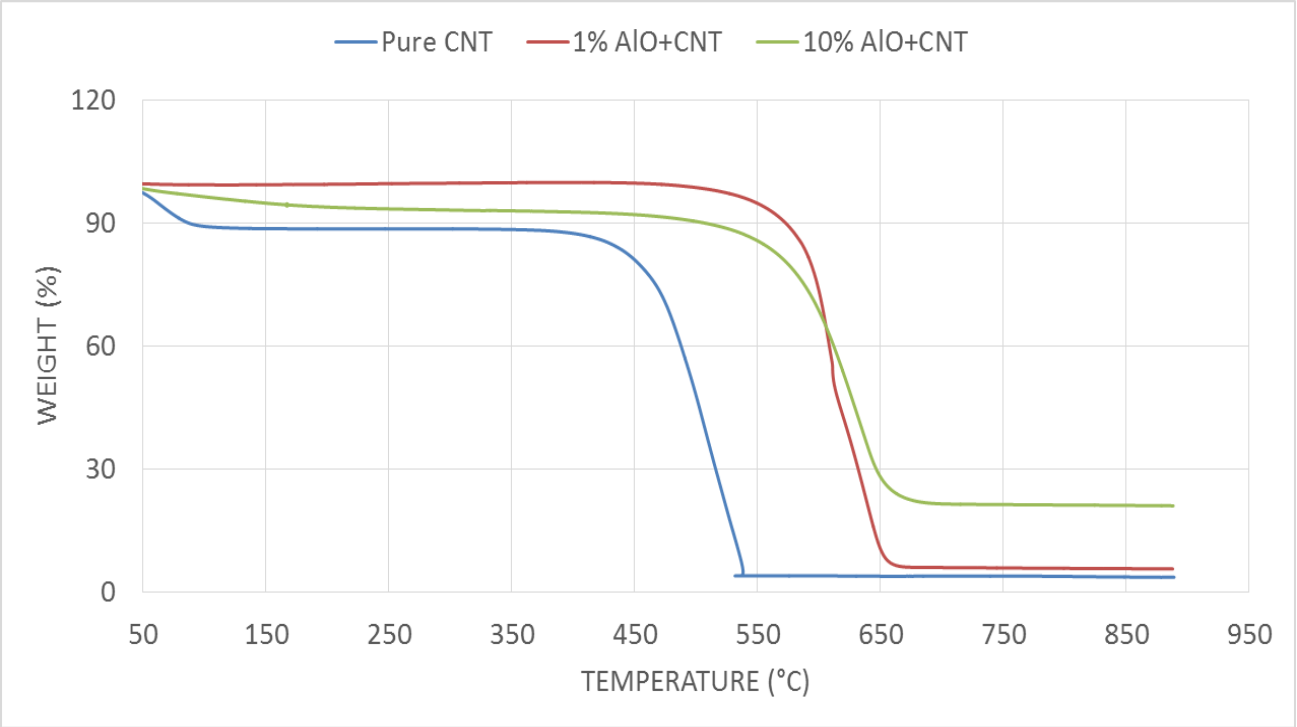

Figure 4.11: CNT + AlO

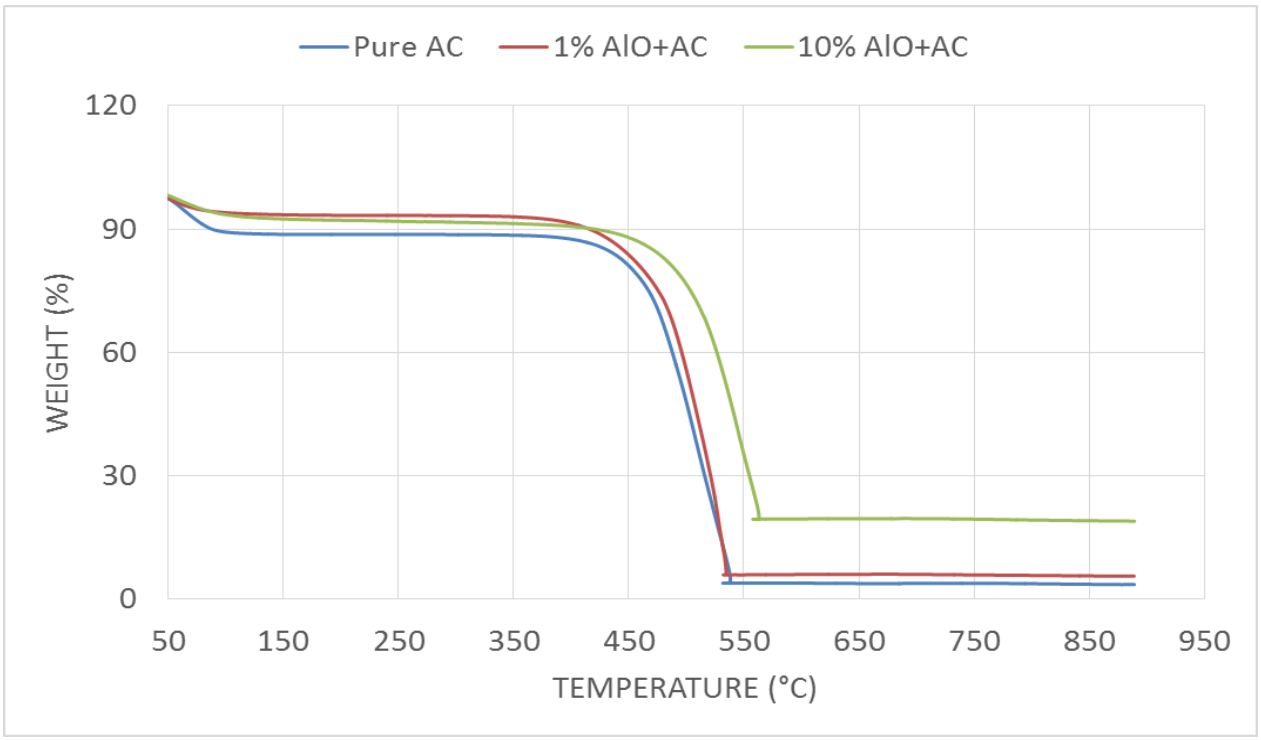

Figure 4.12: AC + AlO

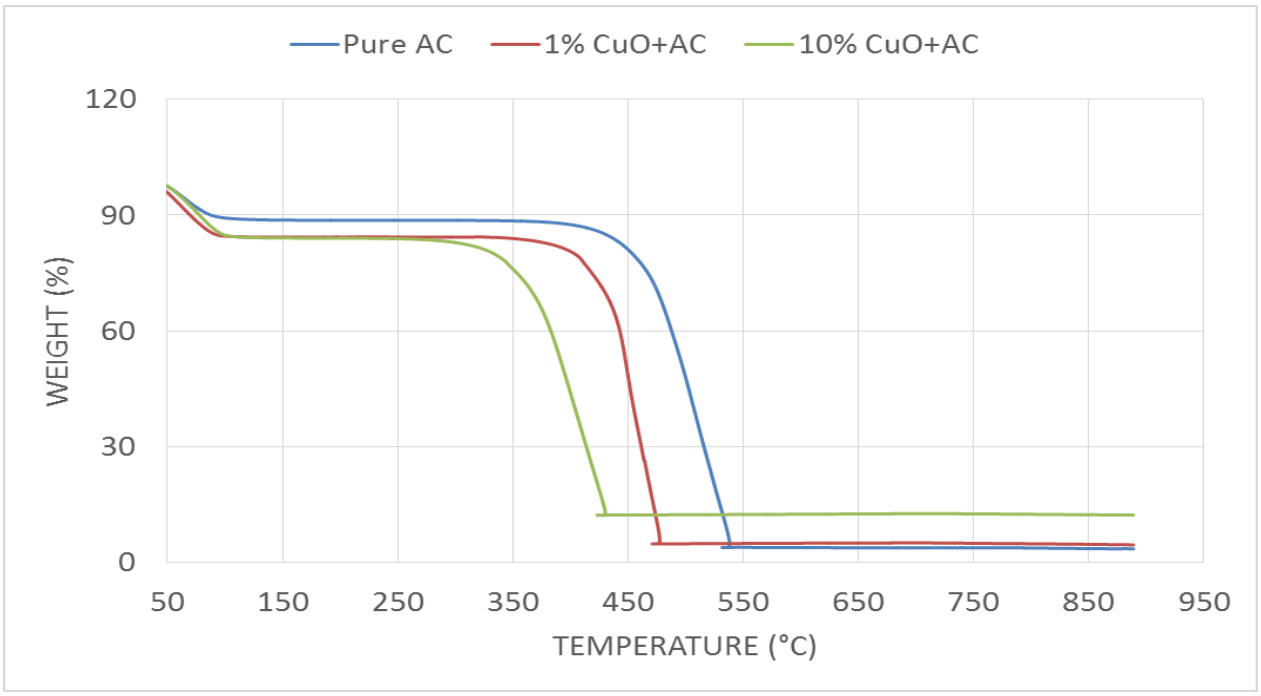

Figure 4.13: AC + CuO

4.2 Removal of Ammonia from Industrial wastewater

Based on the work done in the literature on ammonia removal from waste [47], this study was conducted keeping the foundation of research similar to literature. In addition to raw activated carbon and pure CNT, the materials were further enhanced by impregnating with 4 different metals to see its effect on ammonia removal.

Keeping in mind the conditions of industrial wastewater, many parameters including change in dosage, contact time, agitation speed, pH and temperature were varied in order to optimize the condition. The initial concentration of ammonia stock solution was kept around 200 ppm. The removal percentage of ammonia and adsorption capacity of adsorbent were then calculated.

4.2.1 Effect of pH

Aqua ammonia is classified as week base. In aqua solution, total ammonia consists of 2 forms, ammonia ionized form (NH_4^+) and unionized form (NH_3). It is pH dependent and the equilibrium equation is governed by

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]} = 1.8 \times 10^{-5}\ at\ 25℃$$

When pH is low, equation moves to right and at high pH it moves to left. This study was solely based on the investigation of removal of unionized ammonia (NH_3). The first set of experiment was conducted at 25℃ with 200 RPM, contact time of 2 h. The pH value was varied from 3-11 but according to unionized and ionized ammonia ranges, only pH value from 9-11 were considered for optimizing. If we go beyond pH value 11.5 the ammonium hydroxide ion will be converted to ammonia gas, so natural pH of the solution which was 10.5 was considered as optimized pH value for other parameters study (Ammonia et al., 2000). It is clear from the graph [Figure 4.14] that there is no much effect of pH on removal percentage. 10% Cu impregnation with AC and CNT were considered.

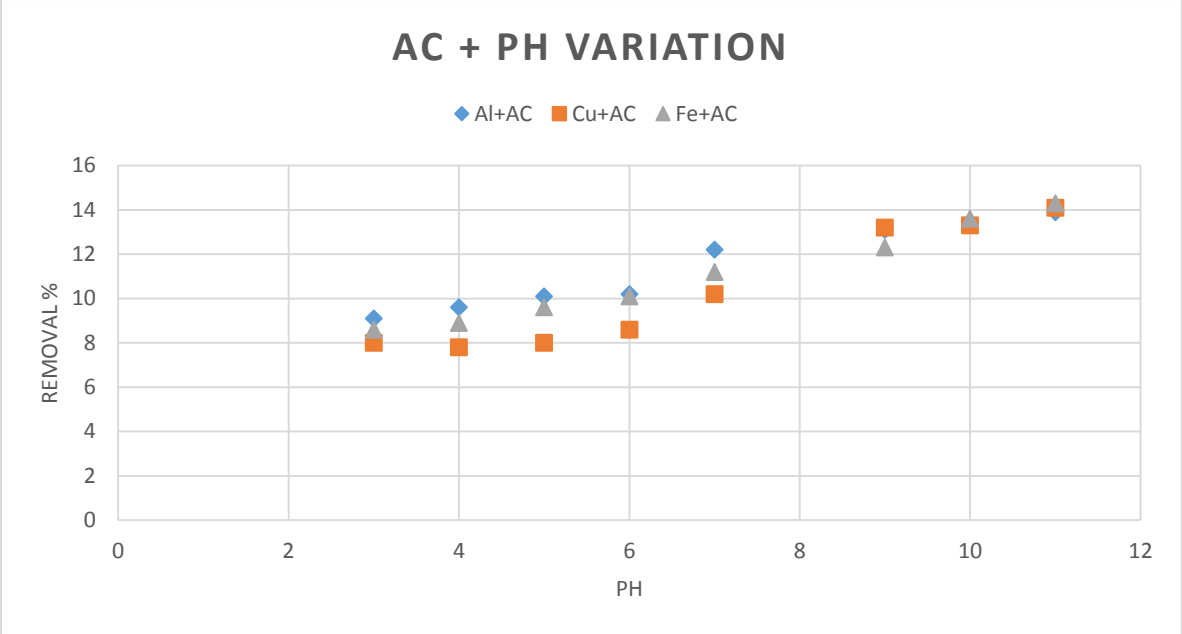

Figure 4.14: Effect of pH on ammonia removal using AC

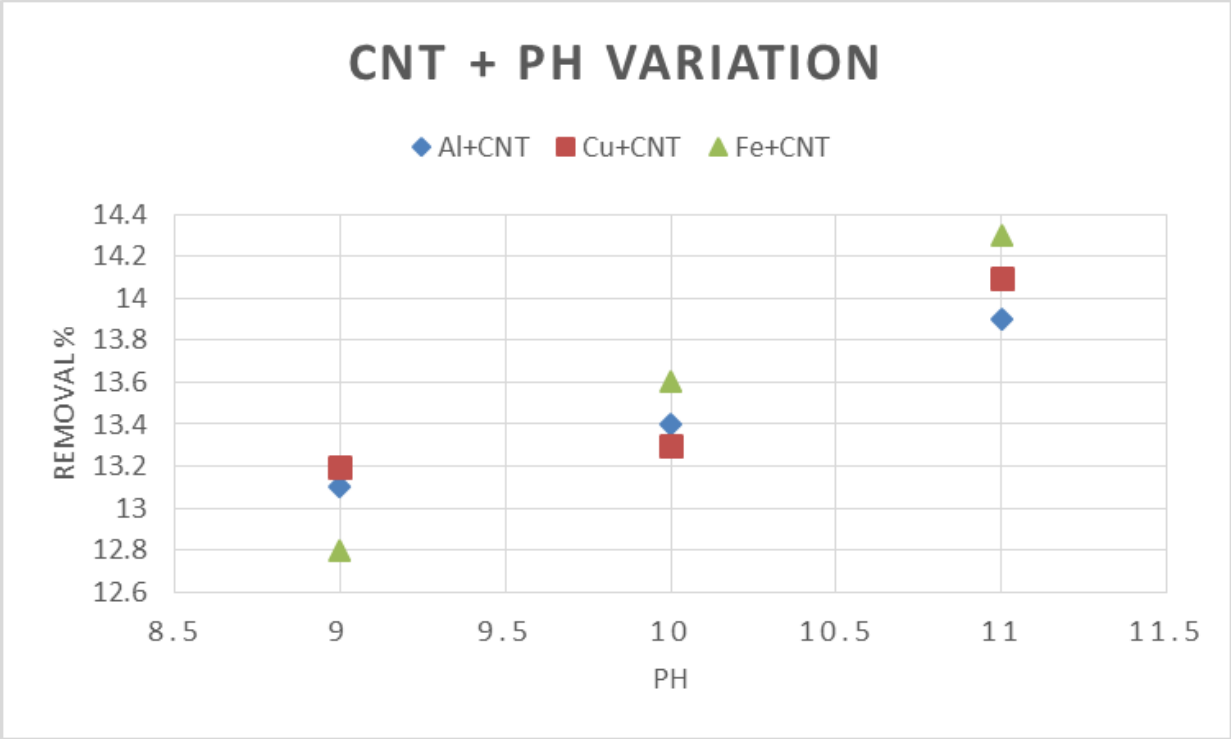

Figure 4.15: Effect of pH on ammonia removal using CNT

4.2.2 Effect of Agitation Speed

After optimizing the value of pH and keeping other constant, the effect of agitation speed was investigated. Value of pH, dosage, temperatures and contact time were fixed at 10.5, 1g, 25℃ and 2 h respectively. By varying the agitation speed from 100 to 250 RPM shown in [Figure 4.16 and Figure 4.17], it can be noticed that the percentage removal increases with the increase in agitation speed. After 200 RPM, the adsorption capacity show equilibrium behavior and removal efficiency as well. Both AC and CNT have shown similar behavior except that overall removal efficiency of AC and its modified versions were higher than its corresponding CNTs

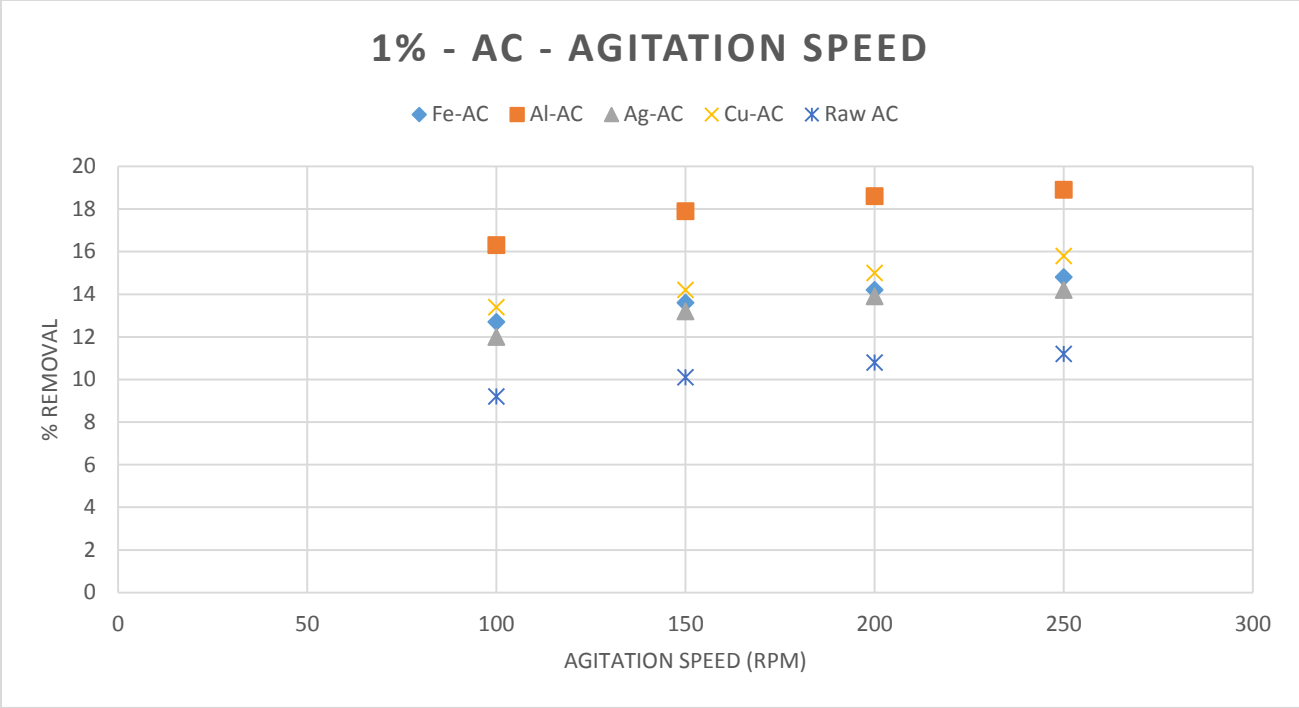

Figure 4.16: Effect of agitation speed on ammonia removal using 1% AC

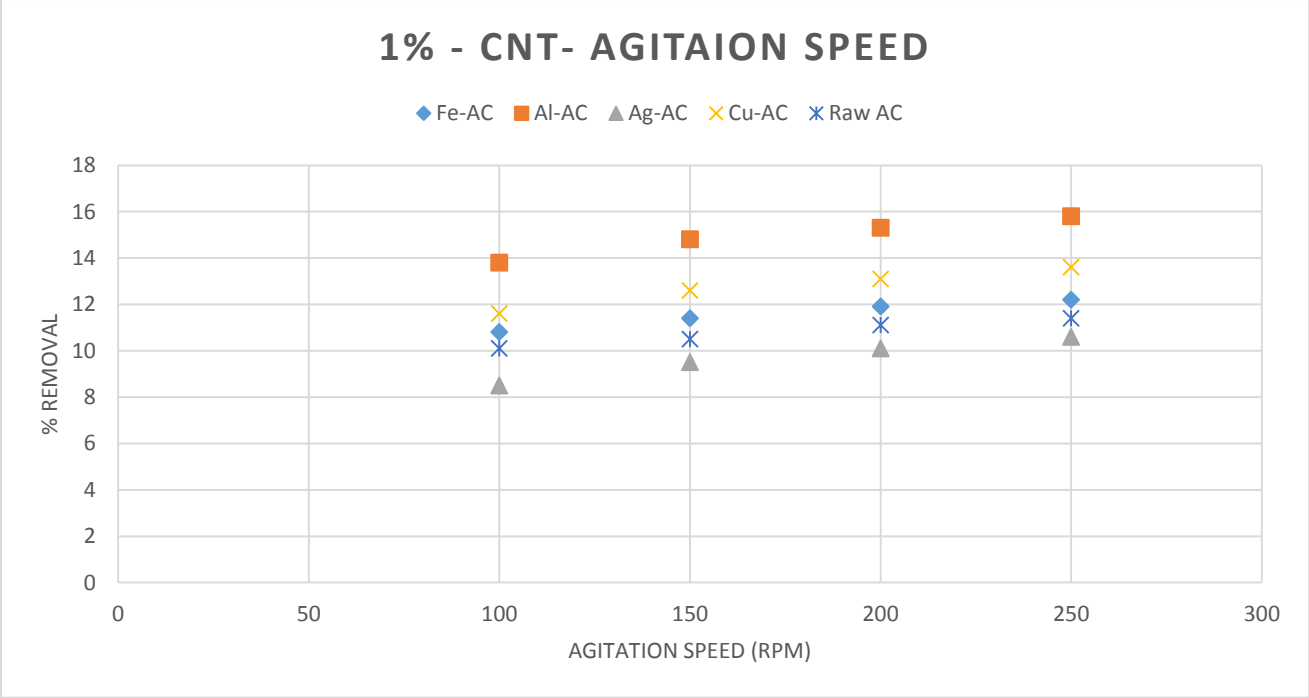

Figure 4.17: Effect of agitation speed on ammonia removal using 1% CNT

The major phenomenon related to this increase in removal percentage with increasing agitation speed keeping other parameter constant is the effect of diffusion of ammonia molecules in the surface of adsorbent. The main resistance for ammonia molecules to adsorb is the H^+ and OH^- ions. When the shaking speed is increased, they have more chance to make contact with the surface binding sites and hence removal increases. External mass transfer is a strong function of surface contact which is increased by the increasing shaking speed. From the results, we conclude that 200 RPM is optimized condition for maximum removal.

Different adsorbent on the basis of their active site binding properties, show different removal percentage. Both AC and CNT were used in its pure state (commercial available) to make a comparison baseline. Two different loading 1% and 10% of impregnation material were taken under consideration.

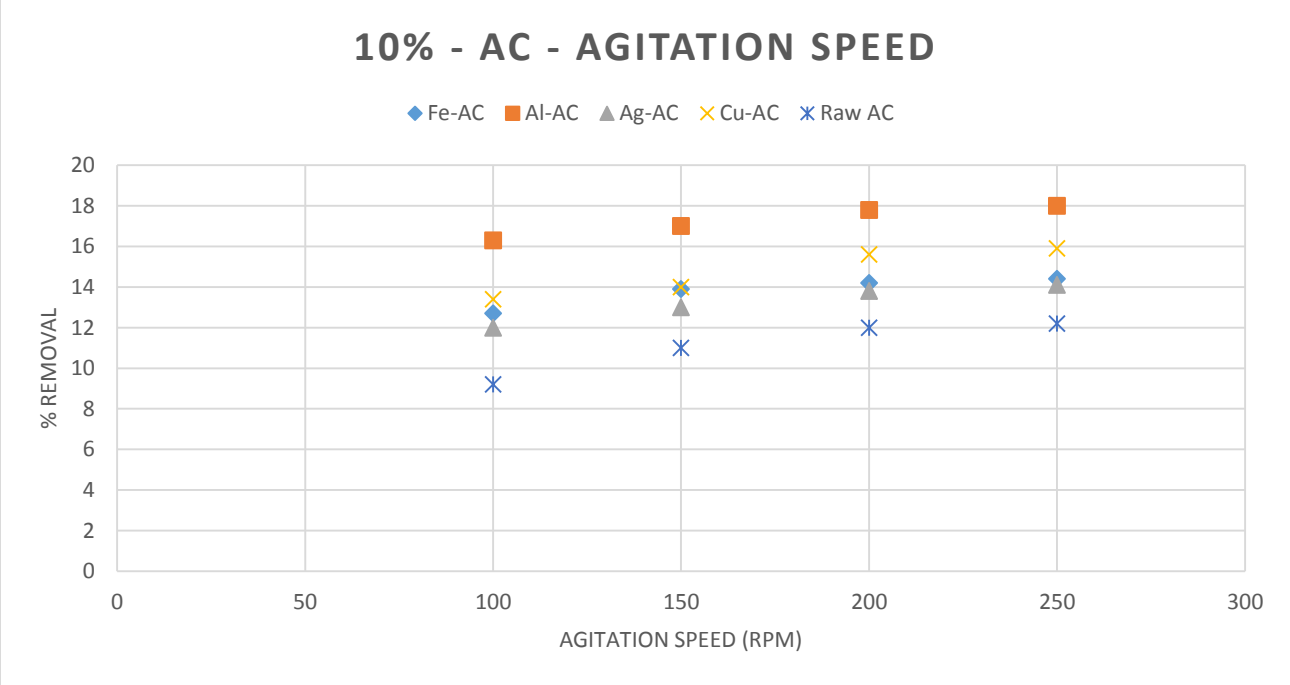

Figure 4.18: Effect of agitation speed on ammonia removal using 10% AC

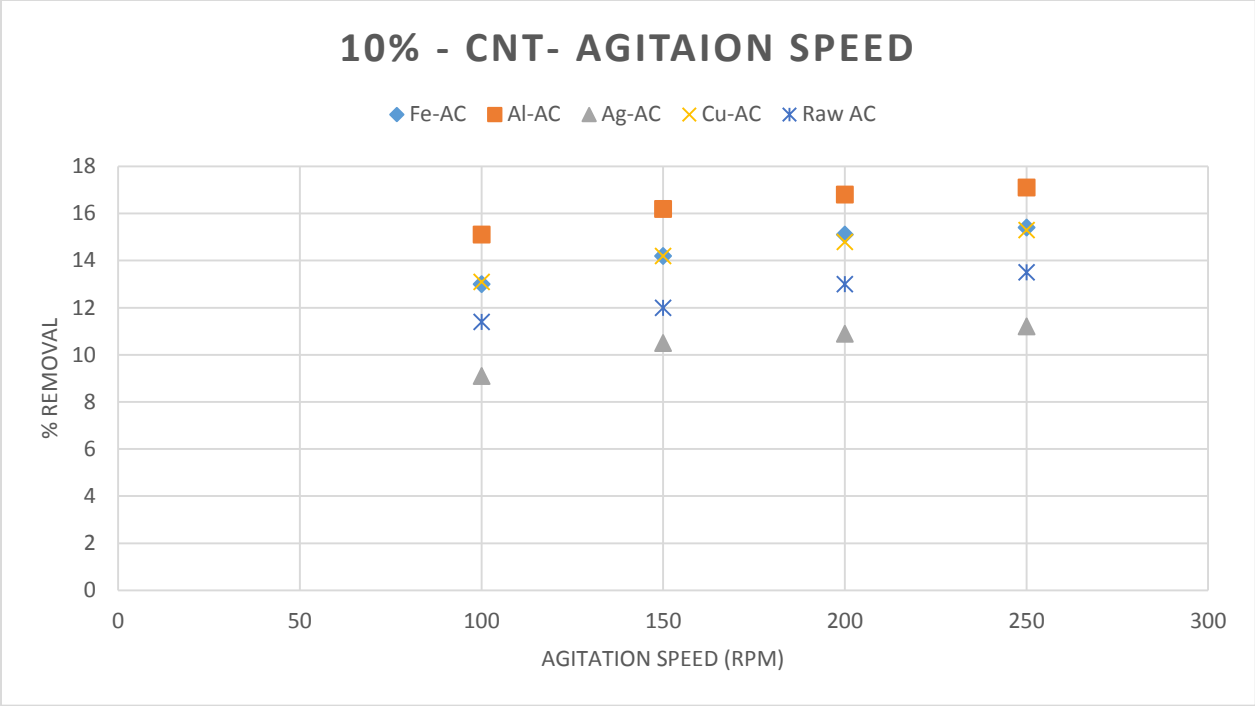

Figure 4.19: Effect of agitation speed on ammonia removal using 10% CNT

From Figure 4.18, it can be interpreted that Al impregnation onto AC has given highest removal. After that Fe and Cu showed better result than pure AC and Ag impregnation. From Figure 4.16 and Figure 4.18, it is clear that 10% loading of material has shown better result that 1% loading due to the presence of more modified active sites on the surface. Similar behavior is noticed by CNT and its modified forms but removal efficiency is lower as compared to AC. All the values are documented in the appendix A.

4.2.3 Effect of Adsorption Dosage

Keeping other parameters pH, contact time, agitation speed and temperature at fixed value of 10.5, 2 h, 200 RPM and 25℃ respectively, adsorption dosage were varied to investigate its effect on ammonia removal.

The basic principle behind the theory is that with the increase in dosage amount of adsorption, there were more active sites available for the molecule to bind with. So, by doing this we increase the exchangeable site for ions.

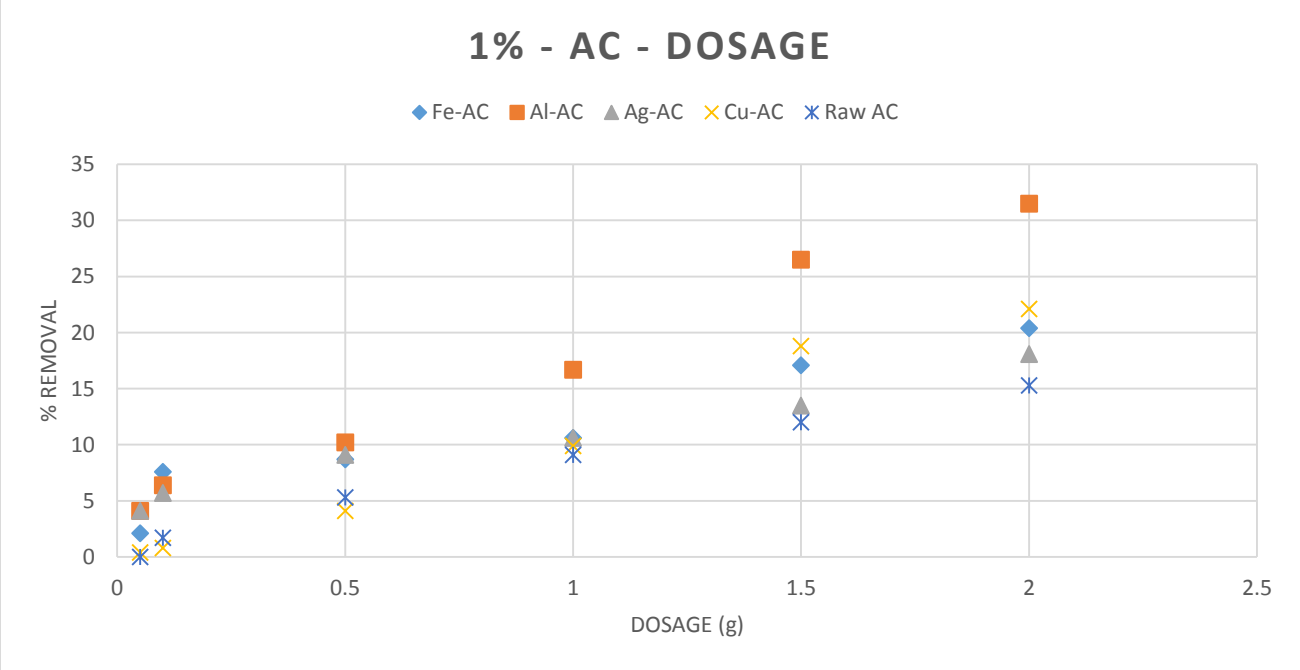

Figure 4.20.: Effect of Dosage on ammonia removal using 1% AC

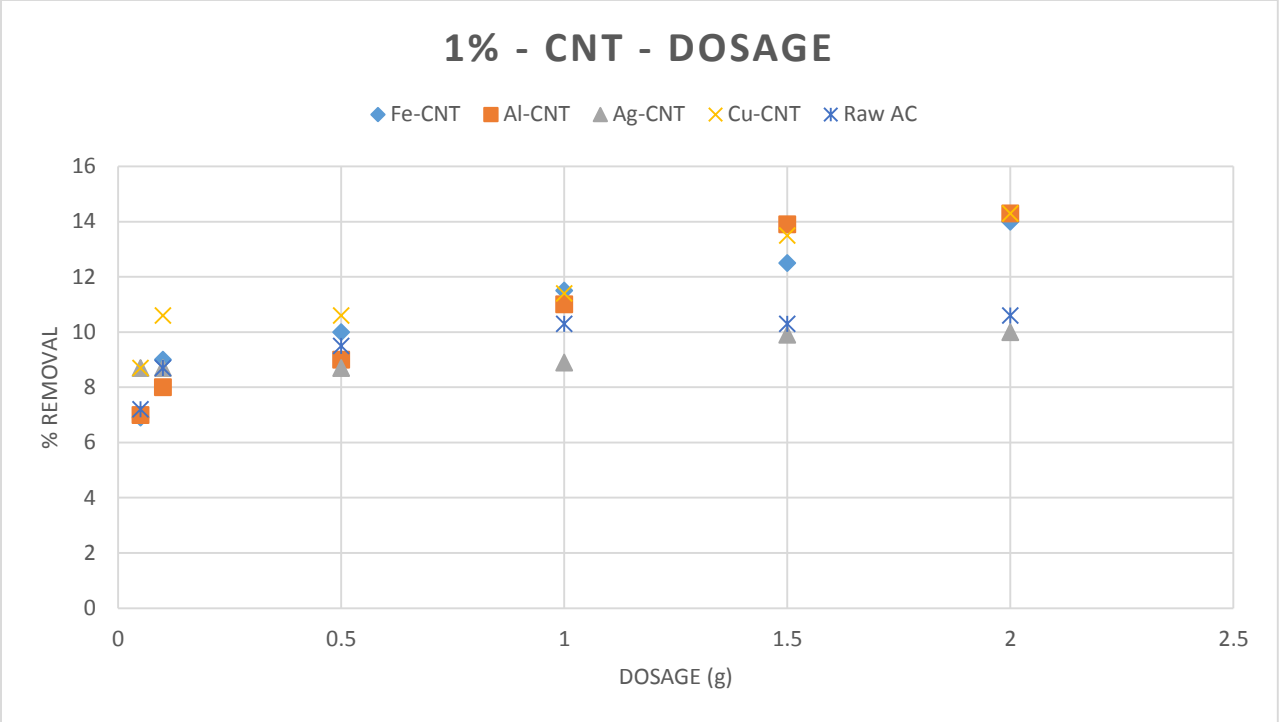

Figure 4.21: Effect of Dosage on ammonia removal using 1% CNT

The amount of dosage used in this case after thorough study of literature [47] was 0.05, 0.1, 0.5, 1 and 2 g of both AC and CNT in 100 ml. It can be seen from the Figure 4.20] that 50 mg (0.05 g) and 100 mg has shown low removal results. It is due to the fact that small amount of dosage is not sufficient to removal high concentration of 200 ppm of ammonia. With the increase in dosage, it was noticed that the removal efficiency started to increase because of availability of more active sites.

Among the activated carbon and its modified version, 10% Al impregnated AC as shown in Figure 4.22, gave the best result with removal percentage of 40.3% followed by Fe impregnation of 37.8% and then Cu for 33.5% at 2 g dosage of adsorbent. Pure and Ag impregnated AC showed much lower results than other. Similar trend was noticed by CNT

and its modified form for both 1% and 10% loading. When comparing 1% and 10% loading of metal, 10% showed better removal results.

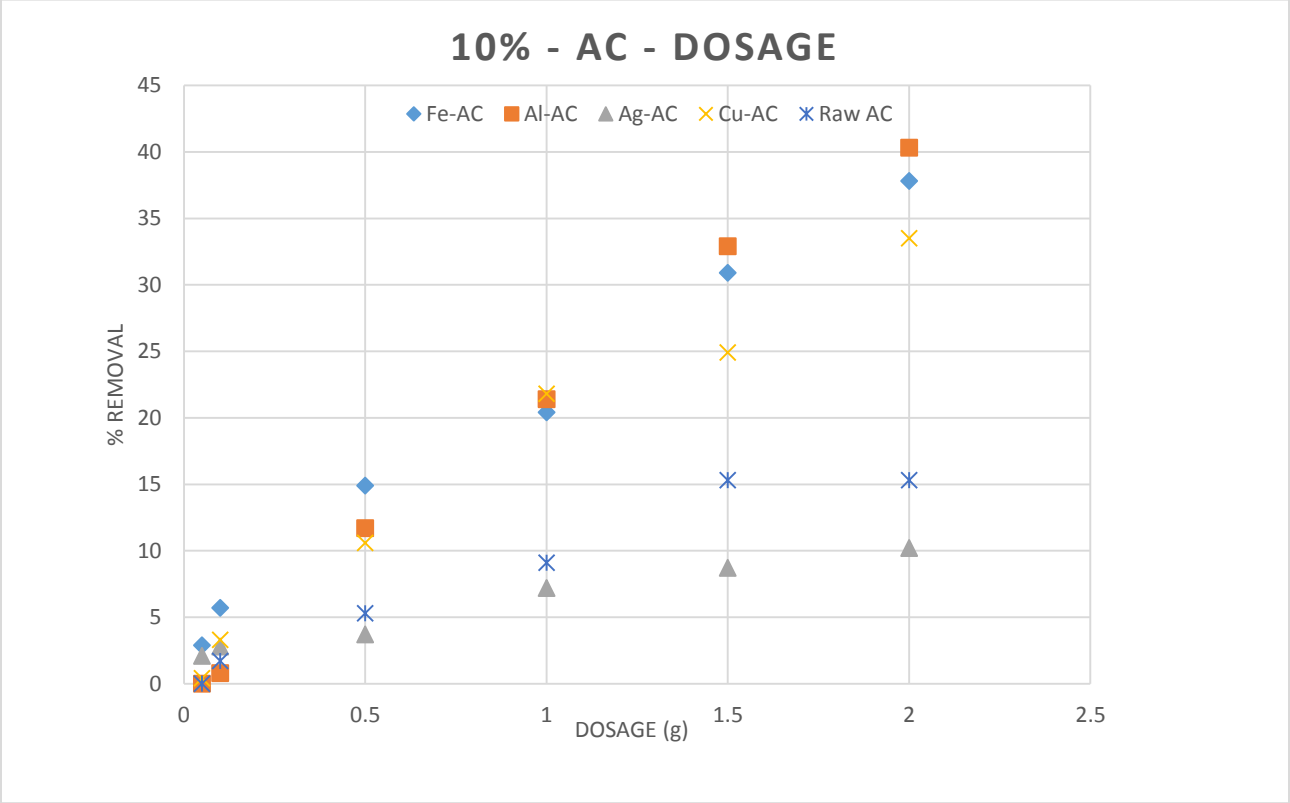

Figure 4.22: Effect of Dosage on ammonia removal using 10% AC

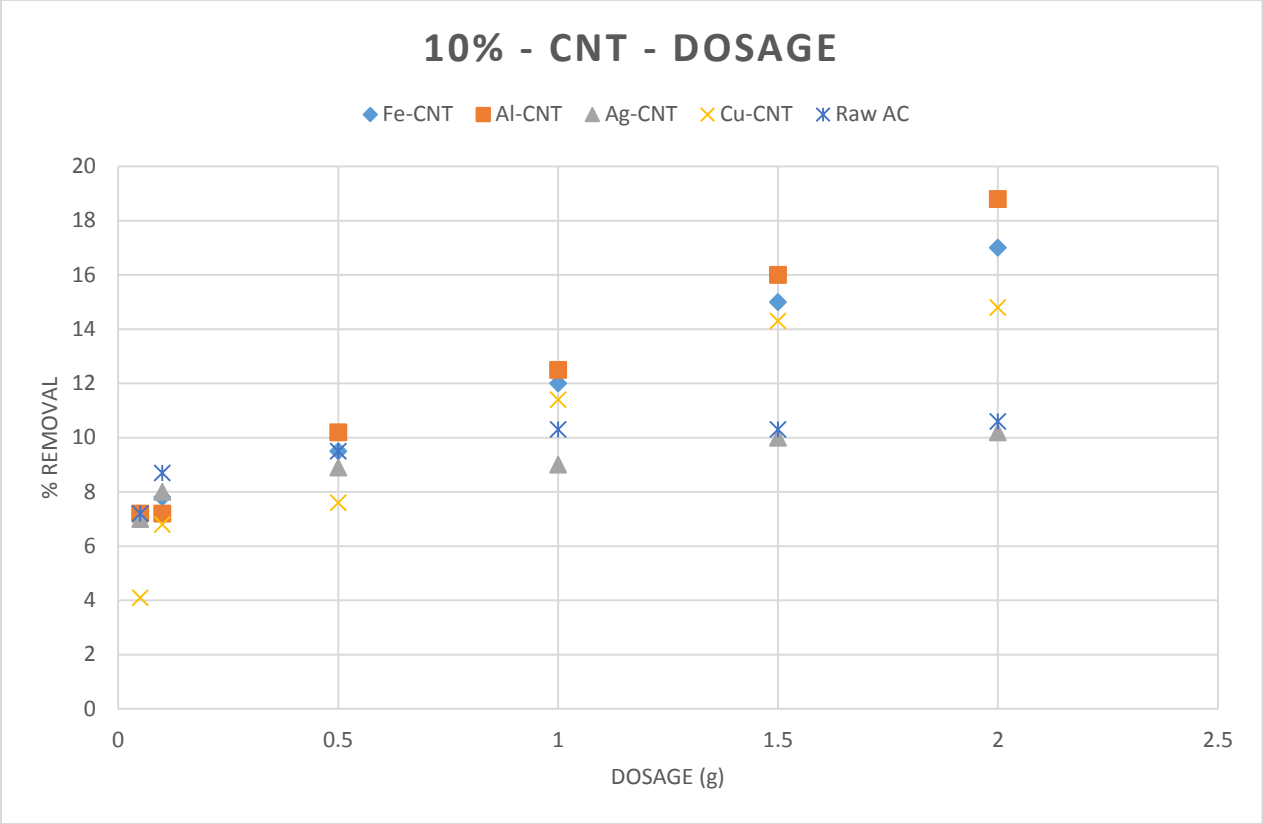

Figure 4.23: Effect of Dosage on ammonia removal using 10% CNT

From the Figure 4.22, it was noticed that even at high dosage of 2 g in 100 ml stock solution, the figure trend do not show equilibrium behavior and has tendency to give higher removal by increasing dosage. But from economic point of view in industries, this amount of dosage will be multiplied many times on larger scale, which might not be economically viable so for experimental investigation the optimize condition 1g adsorbent was considered.

4.2.4 Effect of Contact time

The effect of contact time was investigated at different time intervals keeping the pH, agitation speed, temperature and dosage fixed at 10.5, 200 RPM, 25℃ and 1g respectively. The time interval for contact between adsorbate and adsorbent was varied as 30, 60, 120(2h), 240(4h) and 1440 min (24h).

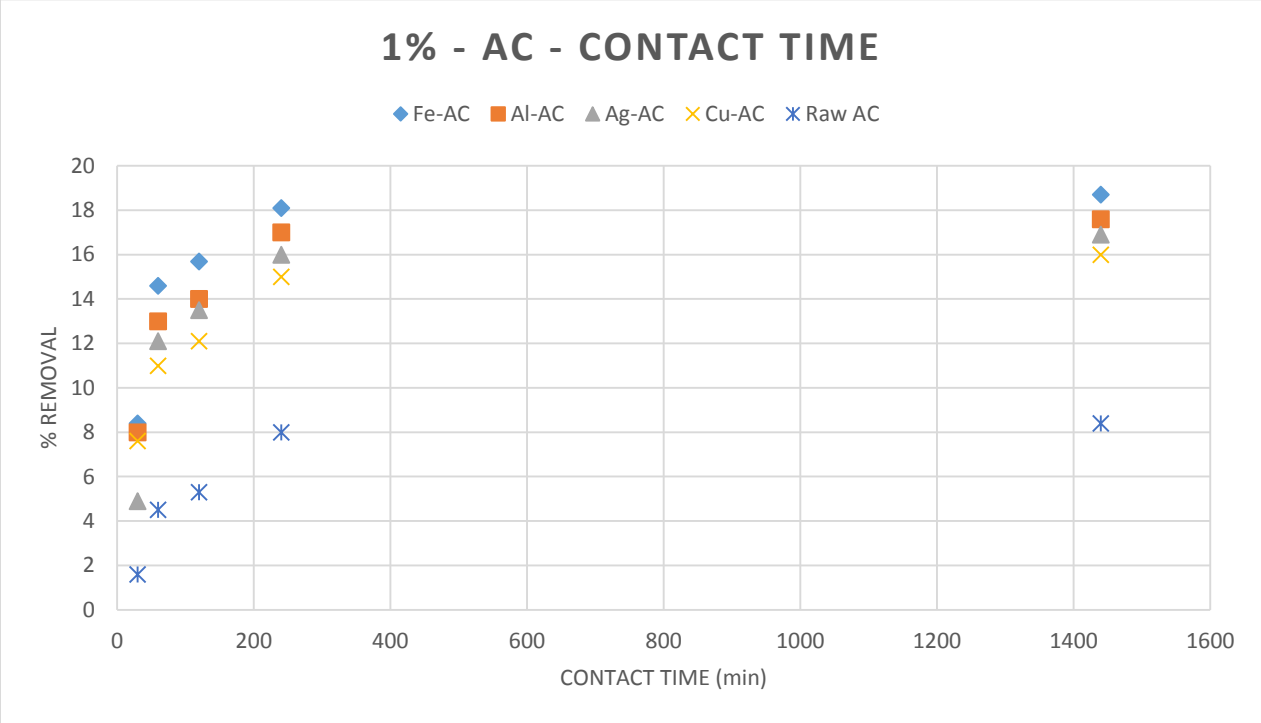

Figure 4.24: Effect of Contact time on ammonia removal using 1% AC

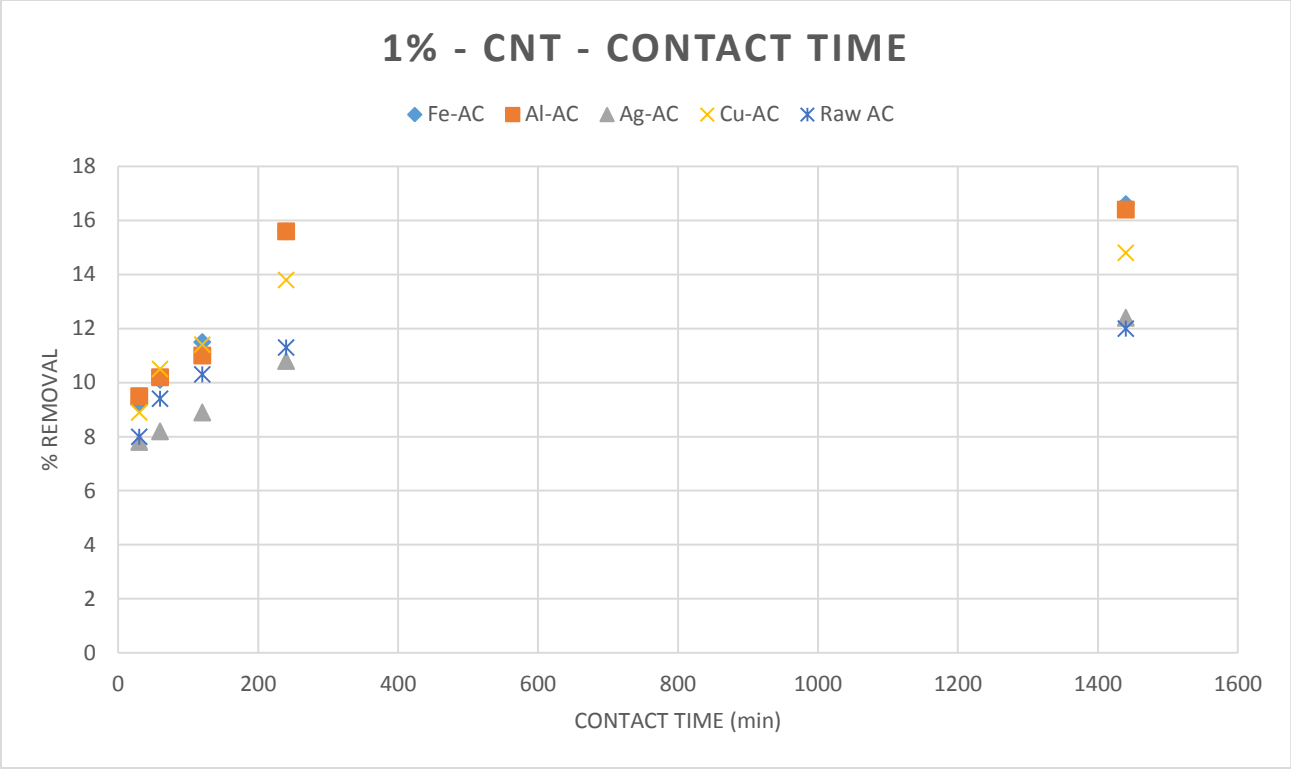

Figure 4.25: Effect of Contact time on ammonia removal using 1% CNT

It can be interpreted from the Figure 4.24 that adsorption rapidly increases in the first 2 h then the trend showed slow removal percentage between 2 h to 4 h and then become constant till 24 h time period. It can be seen that 1% and 10% loading of AC showed much better result than the pure AC. Fe impregnation showed higher removal then followed by Al impregnation.

For CNT, the overall removal percentage was lower than AC for fixed loading (1% or 10%). [Figure 4.27]. Between pure and impregnated CNT, it showed almost similar result as AC with Al and Fe showed higher removal.

The phenomenon behind the study was that of adsorbent and pollutant are allowed to contact for longer time period which allowed them to have more surface exposure and eventually this phenomenon increases the overall removal of ammonia. With the increase in time, more than 4h, the adsorbent gets saturated and equilibrium starts to establish. 2 h contact time between the pollutant and adsorbent was optimized for further study.

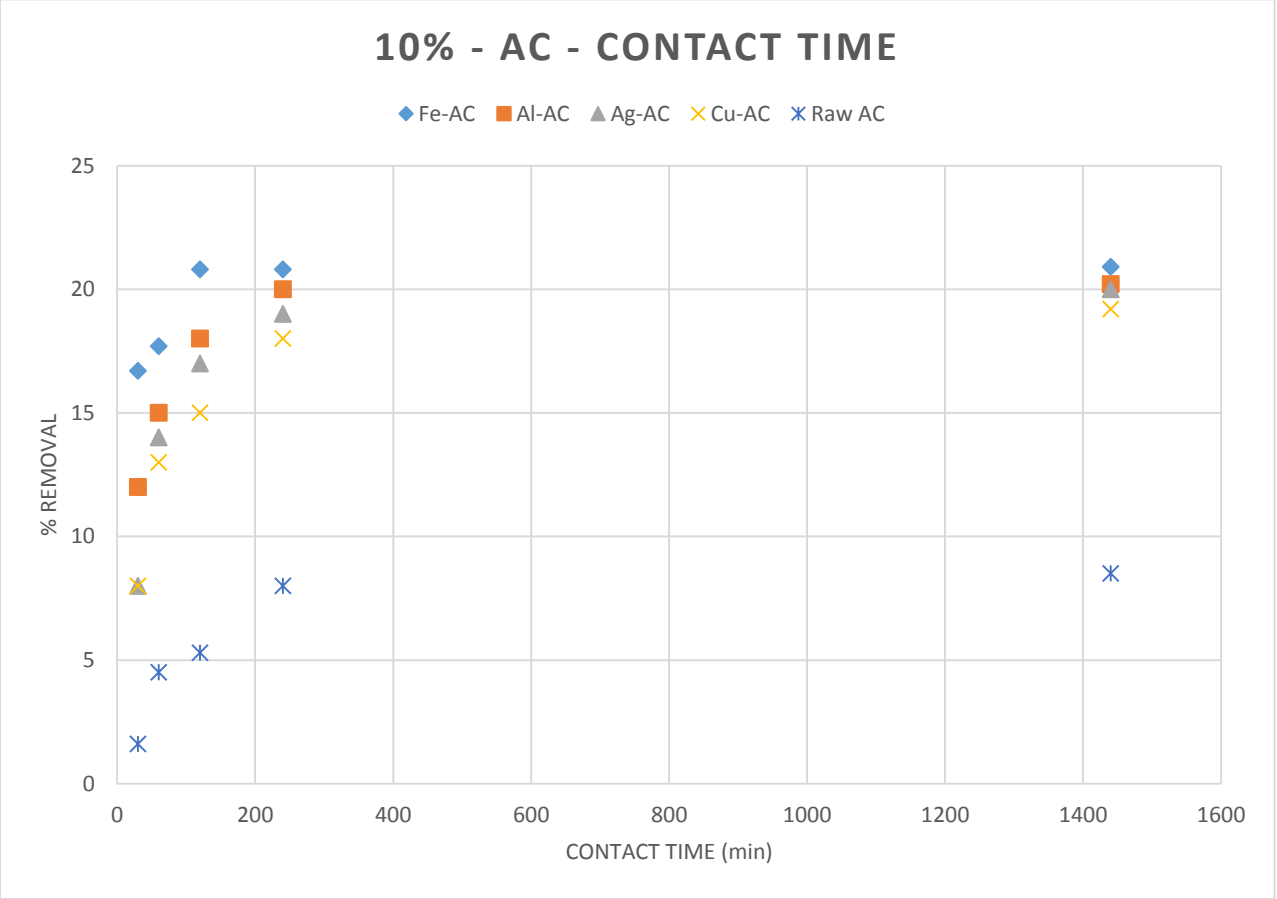

Figure 4.26: Effect of Contact time on ammonia removal using 10% AC

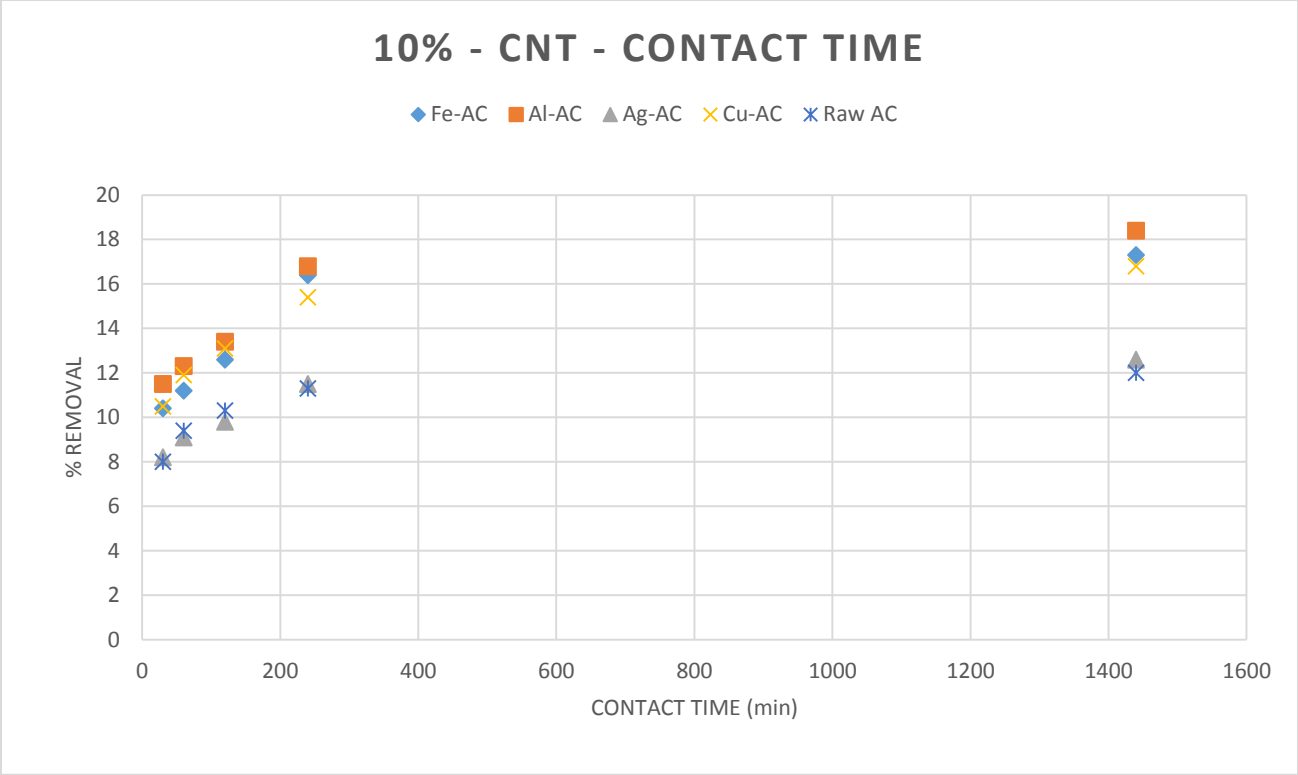

Figure 4.27: Effect of Contact time on ammonia removal using 10% CNT

4.2.5 Effect of Temperature

In this study the temperature was raised in the range of 25℃ to 70℃. All the other parameters pH, dosage, contact time and agitation speed were kept constant at 10.5, 1 g, 2 h and 200 RPM respectively.

The basic principle behind the study was the increased frequency of molecular movement will give more chance for ammonia molecule to interact with adsorption surface. More active sites are accessible with increasing temperature due to increased

movement of molecules, which make the removal percentage to increases. Moreover, with the increasing temperature, the resistance of H^+ and OH^- ions of water are less which increase external mass transfer.

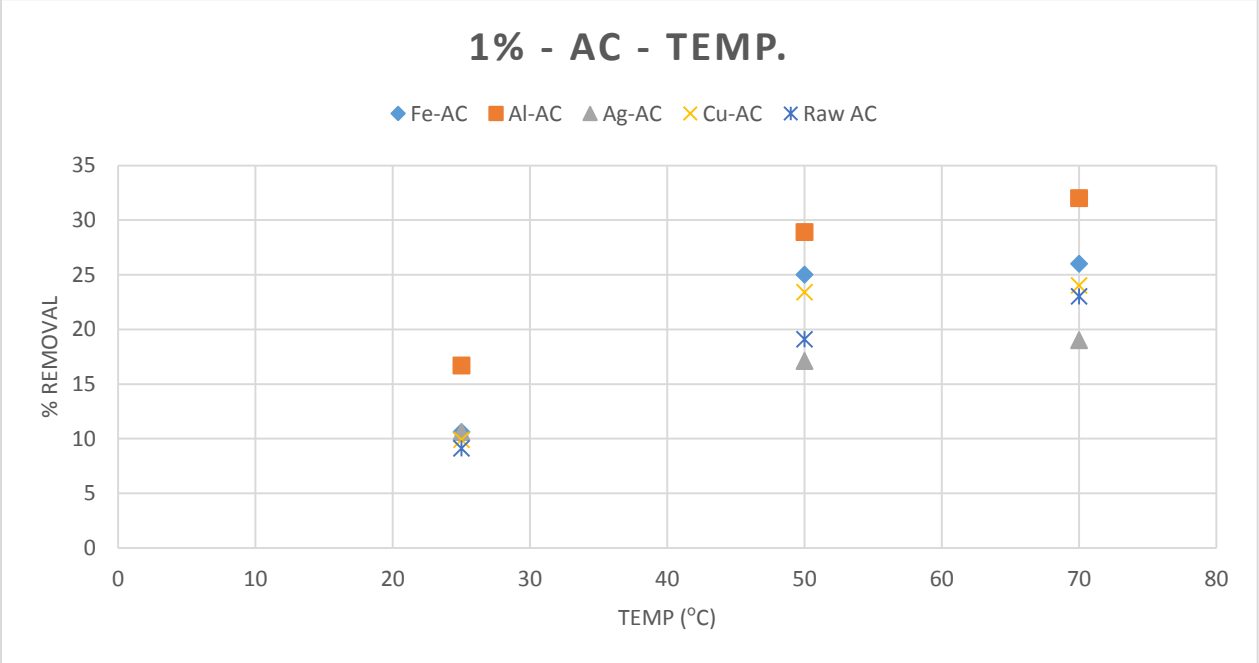

Figure 4.28: Effect of Temperature on ammonia removal using 1% AC

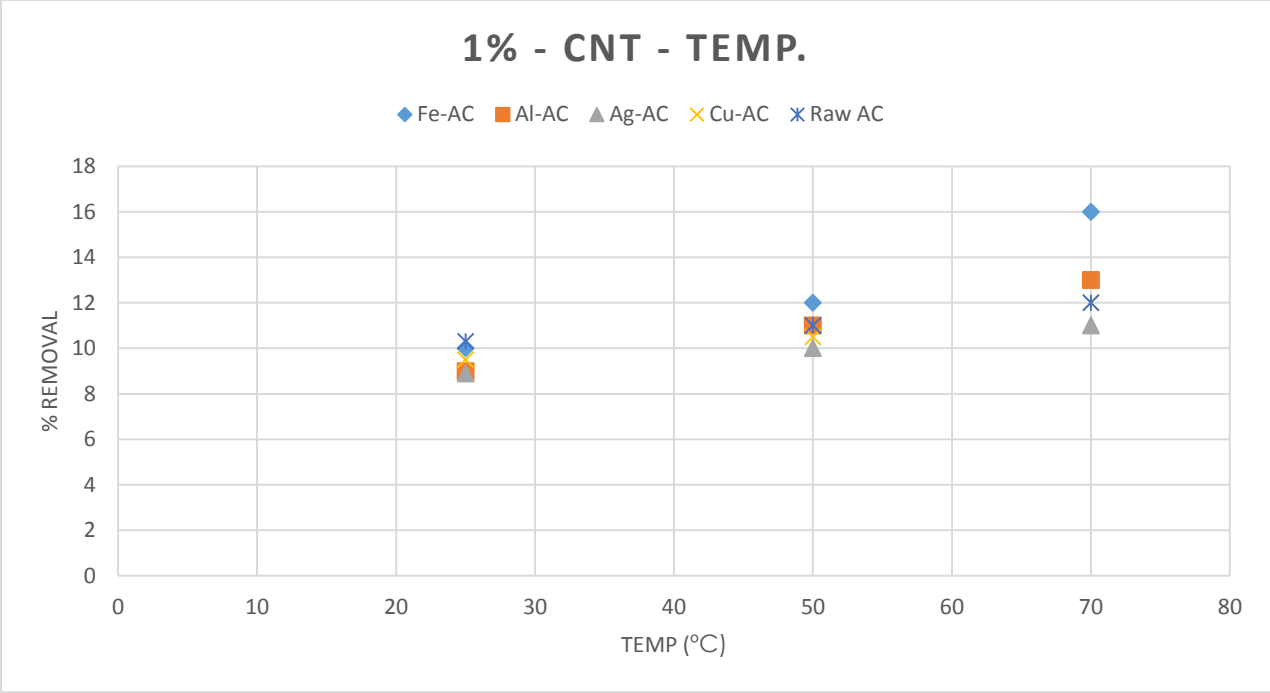

Figure 4.29: Effect of Temperature on ammonia removal using 1% CNT

From the Figure 4.30, it is clear that at temperature 25℃, the removal was within range of 10 – 17%. But with the increase of temperature from 25 to 50℃ and finally to 70℃, the removal efficiency of AC increases to maximum of 32%. In this case also Al and Fe impregnation showed better result than pure and Ag impregnation.

In case of CNT, when temperature was increased from 25 to 50℃, the trend showed slow removal as compared to trend from 50 to 70℃. Loading of 10% showed better removal results than 1%. [Figure 4.29 and Figure 4.31]

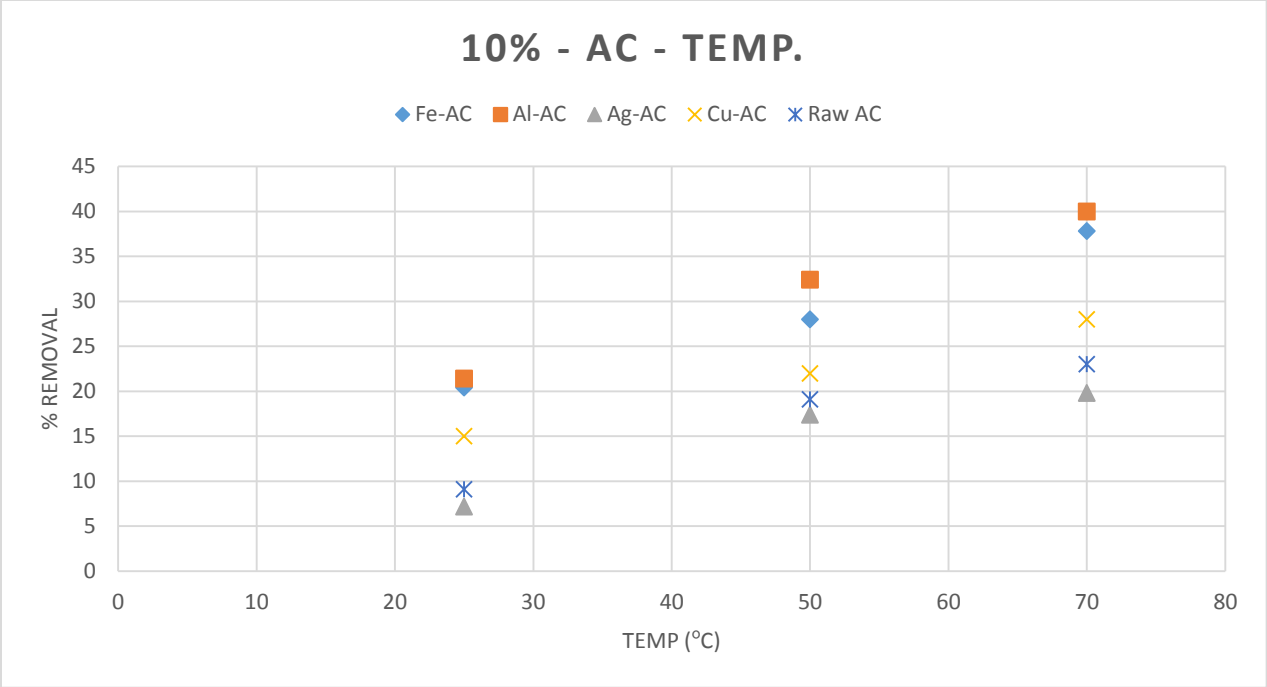

Figure 4.30: Effect of Temperature on ammonia removal using 10% AC

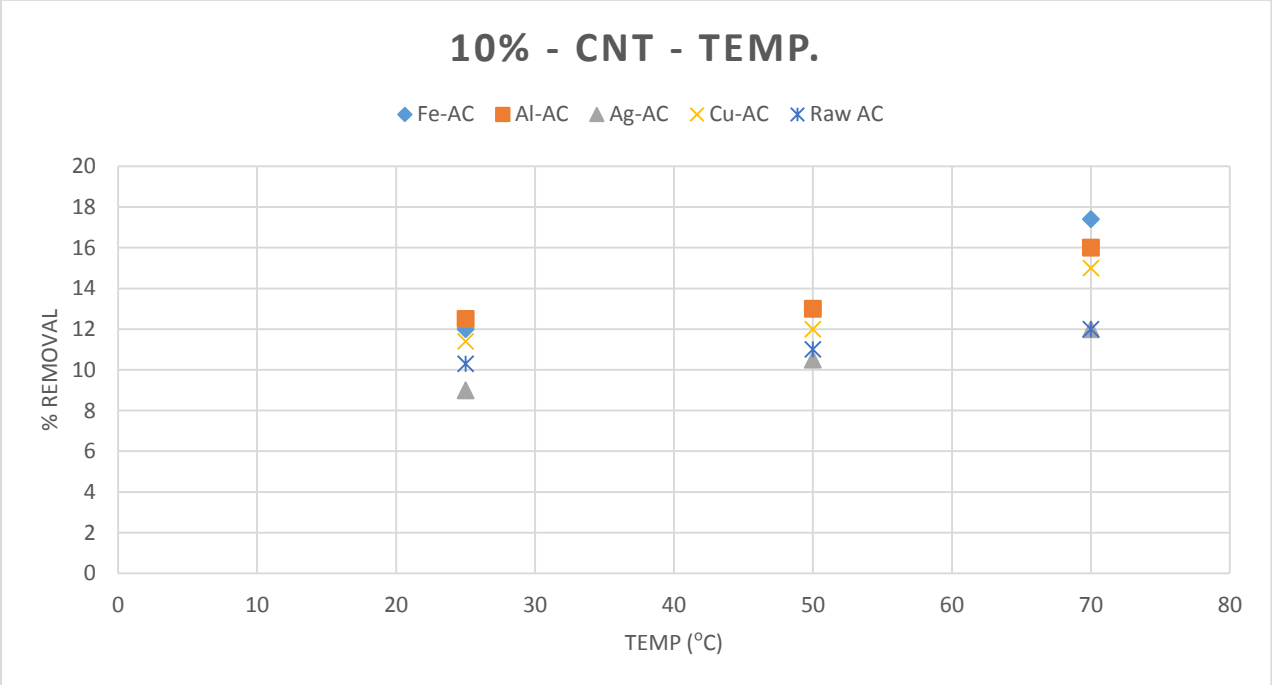

Figure 4.31: Effect of Temperature on ammonia removal using 10% CNT

4.3 Freundlich and Langmuir Isotherm Models

The equilibrium concentration in the fluid phase and the solid phase can be related by several available models, one of the most successful model reported in the literature is Langmuir and Freundlich model.

The Langmuir isotherm model is usually considered the best known of all the isotherms and is defined as

$$Q_e = \frac{Q_m(KC_e)}{(1+KC_e)}$$

Where;

Q_e *= the adsorption density at the equilibrium solute concentration C_e (mg of adsorbate per g of adsorbent)*

C_e *= the equilibrium adsorbate concentration in solution (mg/l)*

Q_m *= the maximum adsorption capacity corresponding to complete monolayer coverage (mg of solute adsorbed per g of adsorbent)*

K *= the Langmuir constant related to energy of adsorption (l of adsorbent per mg of adsorbate)*

The above equation can be rearranged to the following linear form:

$$\frac{C_e}{Q_e} = \frac{\mathbf{1}}{Q_m K} + \frac{C_e}{Q_m}$$

Freundlich model is expressed as:

$$Q_e = K_f (C_e)^{1/n}$$

Where:

Qe **=** *is the adsorption density (mg of adsorbate per g of adsorbent)*

Ce **=** *is the concentration of adsorbate in solution (mg/l)*

Kf *and* ***n*** *are the empirical constants dependent on several environmental factors and* ***n*** *is greater than one.*

This equation is conveniently used in the linear form by taking the logarithm of both sides as:

$$\ln Q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e$$

4.3.1 Adsorption Isotherm Model for Ammonia

At optimized conditions, the evaluation of maximum adsorption capacity was considered. In Figure 4.32 and Figure 4.34, the Langmuir and Freundlich isotherm were used to identify the adsorption capacity Q_m and adsorption intensities from the slope and intercept respectively.

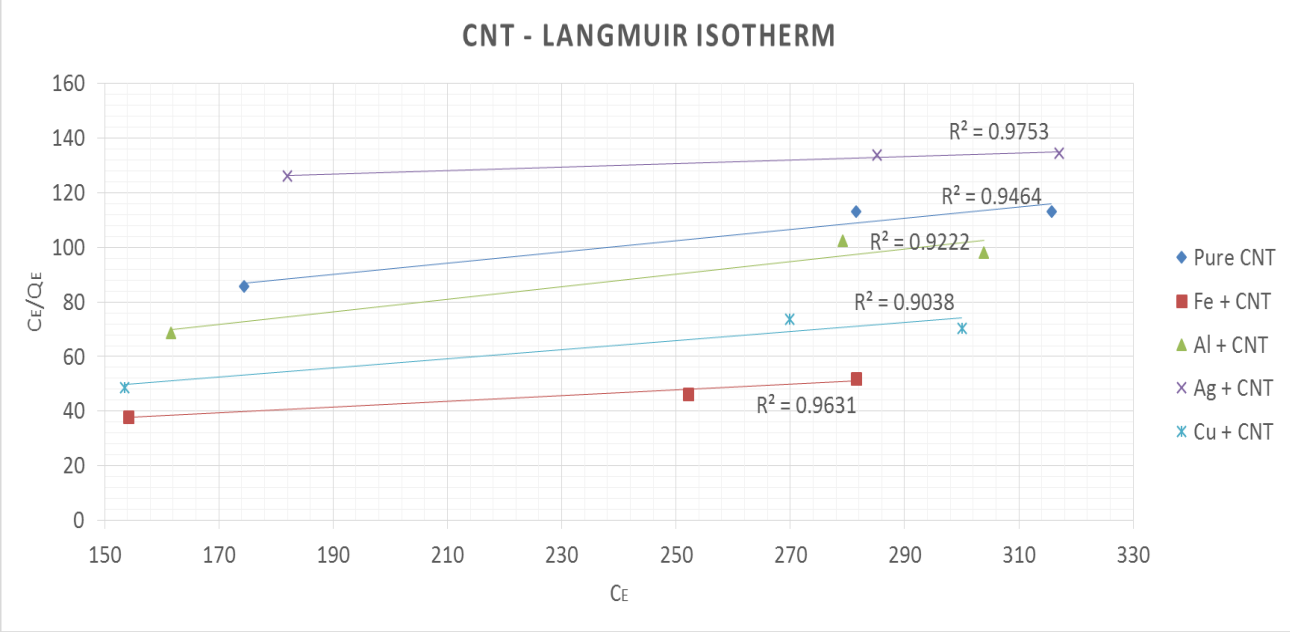

Figure 4.32: Langmuir Adsorption Isotherm model for Ammonia by CNT

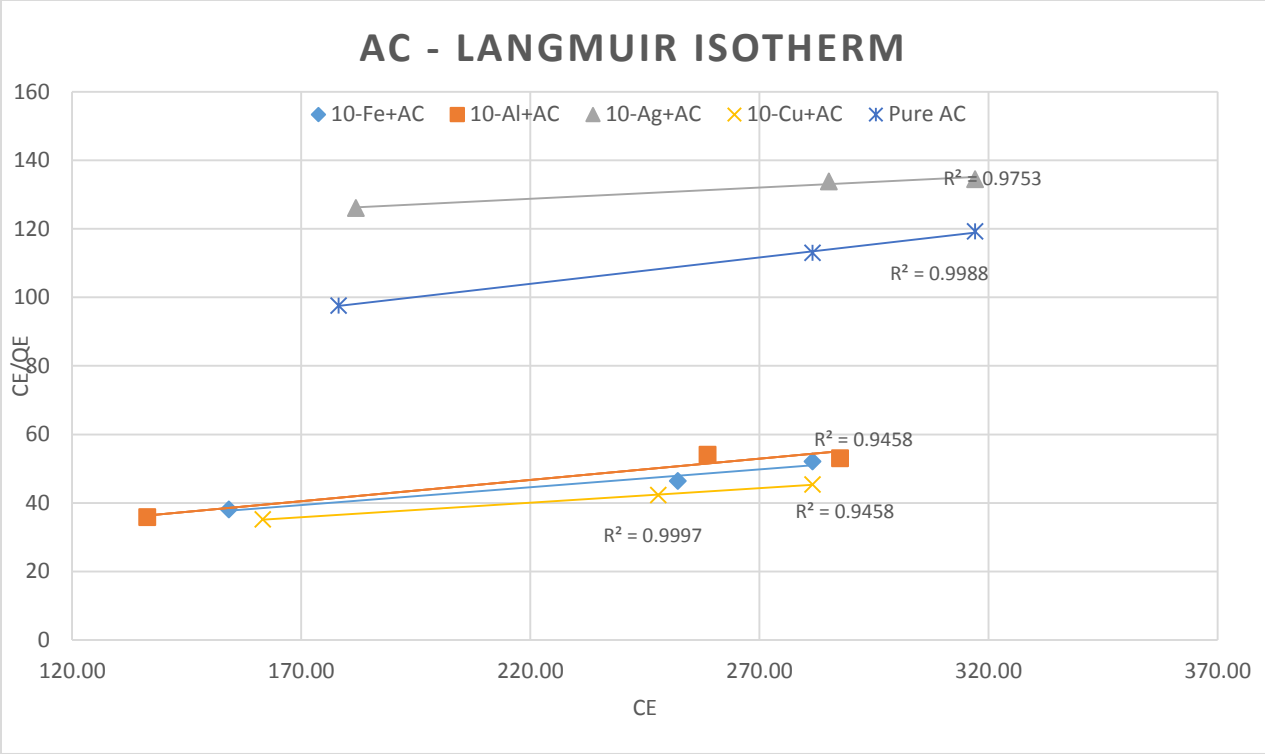

Figure 4.33: Langmuir Adsorption Isotherm model for Ammonia by AC

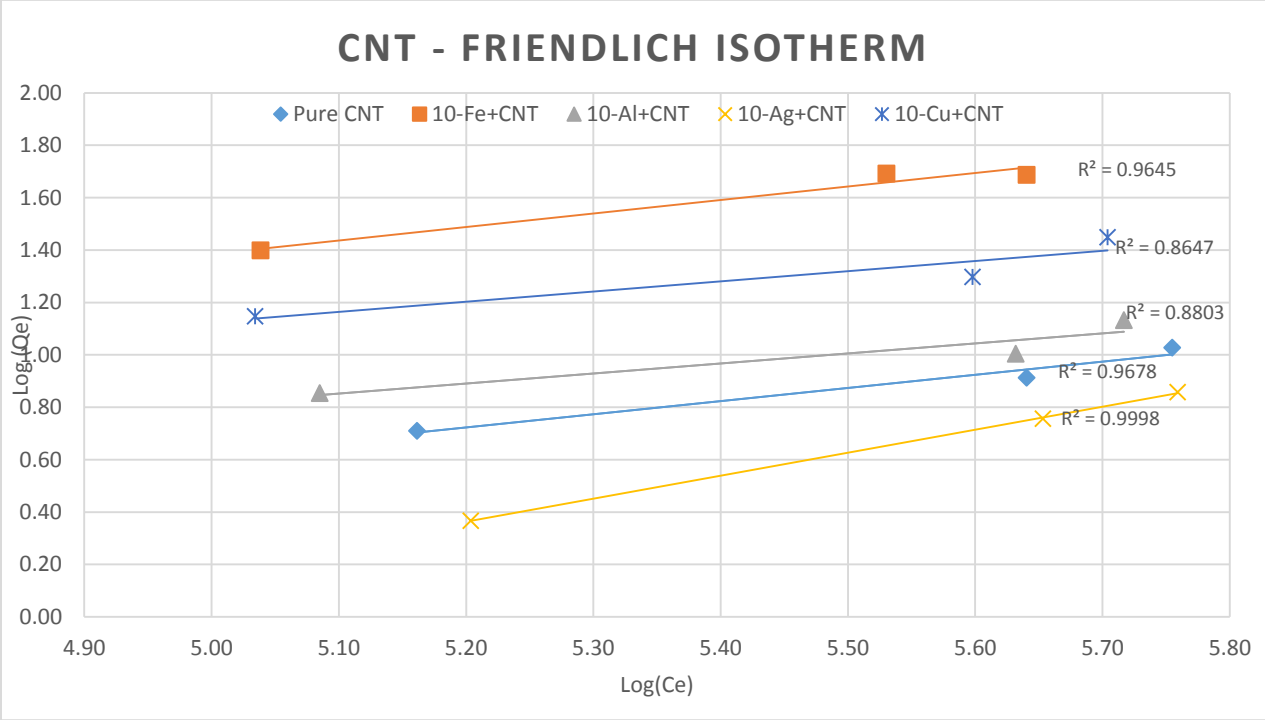

Figure 4.34: Freundlich Adsorption Isotherm model for Ammonia by CNT

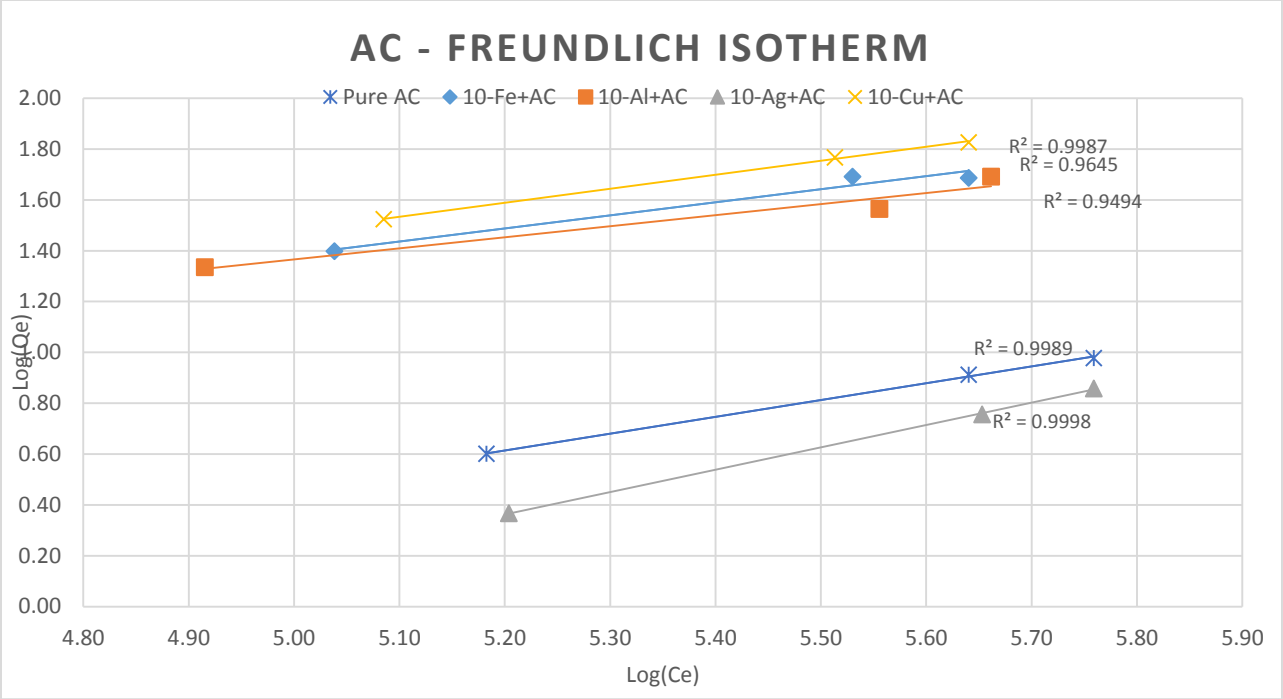

Figure 4.35: Freundlich Adsorption Isotherm model for Ammonia by AC

By comparing the Langmuir and Freundlich isotherm, both are showing good curve fitting by giving correlation factor close to unity. In Table 4.1, the values of correlation factors and values of Q_m and K_L for Langmuir and n and K_F for Freundlich for CNT are shown which are calculated from the slope and intercept respectively for respective isotherms. The values of 1% and 10% are also shown in the table and it can be seen that there is not much difference in contacts between the two loading percentage.

Similar calculation were carried out for Activated Carbon and its impregnated forms. The curve fitting for both Langmuir and Freundlich showed good correlation factors. In Table 4.2 it can be seen that 1% and 10% loading has also shown not much

difference in values. The value of Q_m, n and adsorption intensities were calculated from slope and intercepts.

Table 4.1: Langmuir and Freundlich Isotherm Parameters for Impregnated CNT

	Langmuir			Freundlich		
Adsorbent	Q_m (mg/g)	K_L	R^2	n	K_F	R^2
Pure CNT	6.23	0.773	0.9464	1.986	0.150	0.9678
1% Fe+ CNT	1.322	-1.293	0.9982	0.378	2.15	0.991
1% Al+ CNT	1.351	-1.26	0.9787	0.375	1.73	0.9984
1% Ag+ CNT	1.253	-1.299	0.9883	0.401	3.67	0.9728
1% Cu+ CNT	3.714	-10.19	0.9982	0.927	8.79	1
10% Fe+ CNT	12.96	0.741	0.9631	1.943	0.304	0.9645
10% Al+ CNT	9.314	0.4669	0.9222	2.619	0.334	0.8803
10% Ag+ CNT	2.72	5.515	0.9753	1.137	0.014	0.9998
10% Cu+ CNT	12.49	0.479	0.9038	2.57	0.44	0.8647

Table 4.2: Langmuir and Freundlich Isotherm Parameters for Impregnated AC

	Langmuir			Freundlich		
Adsorbent	Q_m (mg/g)	K_L	R^2	n	K_F	R^2
Pure AC	4.525	1.434	0.9988	1.513	0.06	0.9989
1% Fe+ AC	1.715	-1.393	0.9982	0.378	2.15	0.991
1% Al+ AC	8.040	1.706	0.9488	1.41	0.09	0.9881
1% Ag+ AC	1.948	-1.227	0.9995	0.39	3.89	0.9978
1% Cu+ AC	1.435	-1.285	1	0.342	4.45	0.9953
10% Fe+ AC	12.96	0.707	0.9997	1.942	0.30	0.9645
10% Al+ AC	14.765	0.546	0.9631	2.29	0.44	0.9494
10% Ag+ AC	2.772	5.515	0.9753	1.137	0.014	0.9998
10% Cu+ AC	0.906	13.077	0.9458	1.820	0.282	0.9987

4.4 Modeling of Kinetic Adsorption

In industrial applications of adsorption, kinetic modelling plays an important role in comparing different materials under different conditions. In this study, kinetics of ammonia was investigated using experimental data during time interval from 30 min to 1440 min (24 hr).

The models which were used for kinetic investigation were second order kinetic model and pseudo second order kinetic model. Respective values of Q_e and K_s were calculated from slope and intercept. Below are their equations and linearize form.

1. The pseudo – second order rate equation:

   $$\frac{t}{Q_t} = \frac{1}{2K_s Q_e^2} + \frac{t}{Q_s}$$

   The calculated quantities $\frac{t}{Q_t}$ will be plotted versus time (t)

2. The second order rate equation:

   $$\frac{1}{Q_e - Q_t} = \frac{1}{Q_e} + K_2 t$$

   The calculated quantity $\left(\frac{1}{Q_e - Q_t}\right)$ will be plotted versus time (t)

Where:

Qe = sorption capacity at equilibrium

Qt = sorption capacity at time (mg/g)

KL = the Lagergren rate constant of adsorption (1/min)

K2 = rate constant of the pseudo second-order sorption ($g.mg^{-1}.min^{-1}$)

t = time (min)

4.4.1 Kinetic Adsorption Model for Ammonia

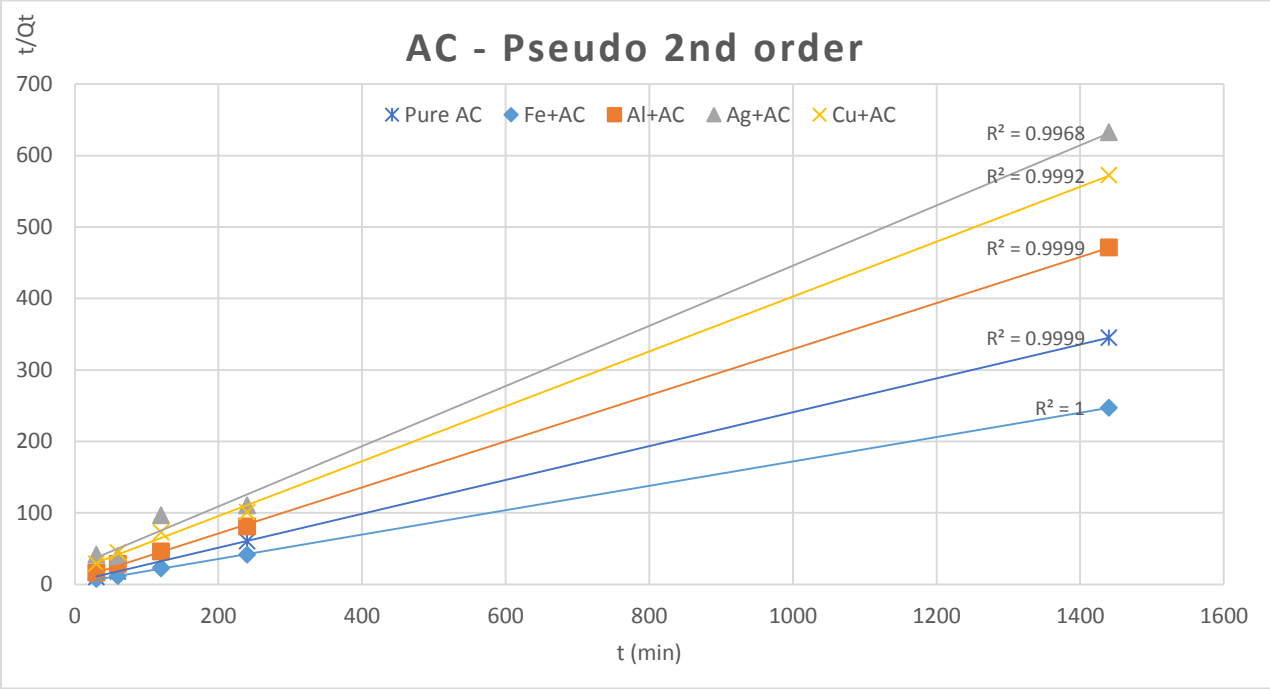

Figure 4.36: Pseudo 2nd Order Kinetic model for Removal of Ammonia by Impregnated AC

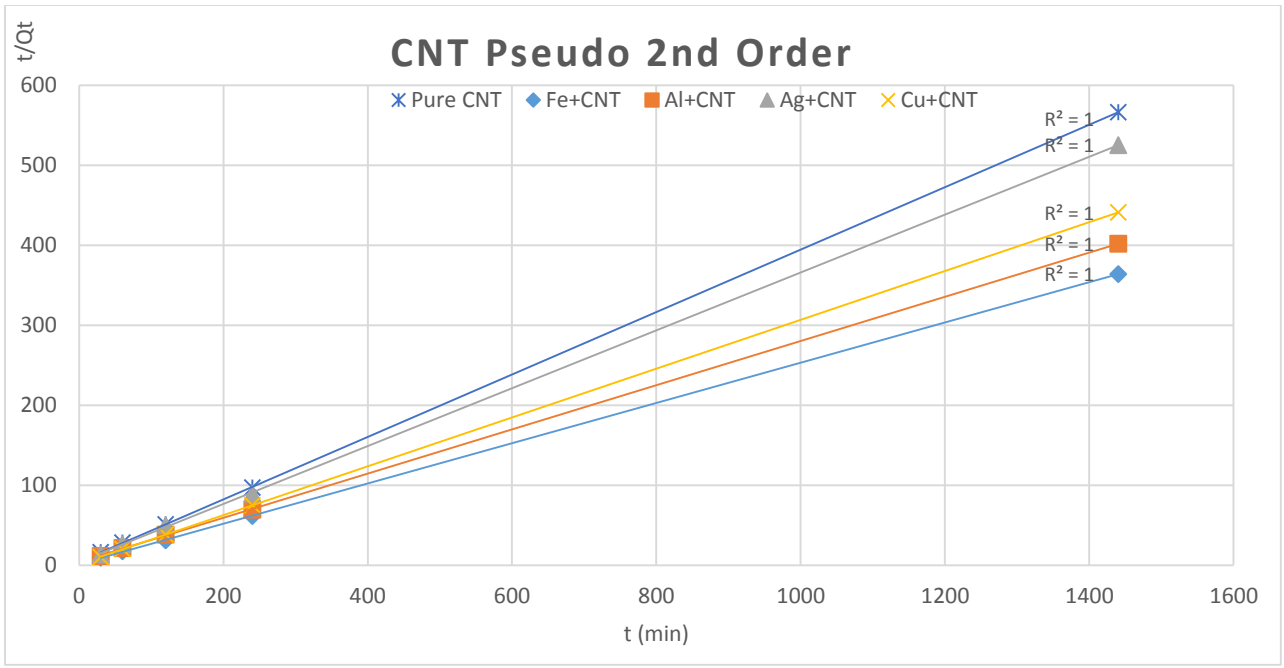

Figure 4.37: Pseudo 2nd Order Kinetic model for Removal of Ammonia by Impregnated CNT

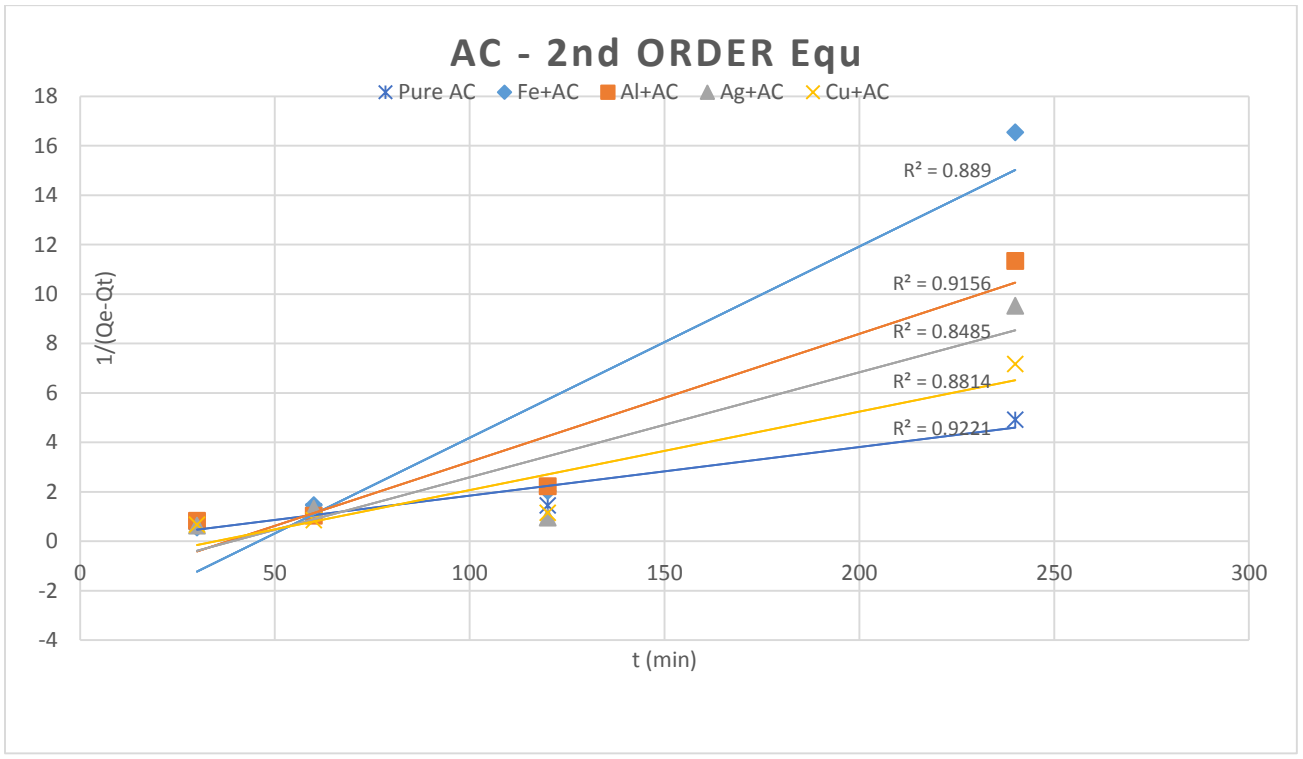

Figure 4.38: 2nd Order Kinetic model for Removal of Ammonia by Impregnated AC

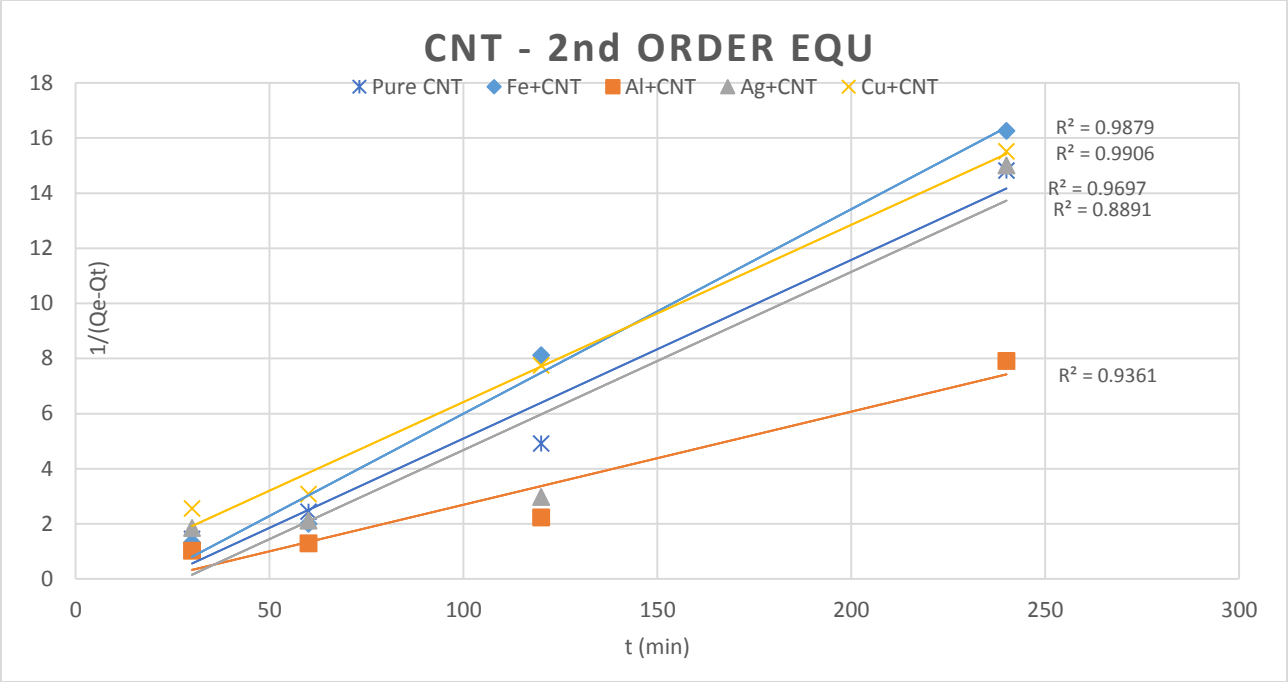

Figure 4.39: 2nd Order Kinetic model for Removal of Ammonia by Impregnated AC

Table 4.3: Kinetic Parameters for Impregnated AC

	Pseudo 2nd Order			2nd Order		
Adsorbent	Q_e (mg/g)	K_s	R^2	Q_e (mg/g)	K_2	R^2
Pure AC	4.22	0.00678	0.9999	8.264	0.0197	0.9221
10% Fe+ AC	5.871	0.00873	1	0.281	0.0773	0.889
10% Al+ AC	3.102	0.0076	0.9999	0.5088	0.0518	0.9156
10% Ag+ AC	2.374	0.00356	0.9968	0.600	0.0425	0.8485
10% Cu+ AC	2.604	0.00391	0.9992	0.9015	0.0318	0.8814

Table 4.4: Kinetic Parameters for Impregnated CNT

	Pseudo 2nd Order			2nd Order		
Adsorbent	Q_e (mg/g)	K_s	R^2	Q_e (mg/g)	K_2	R^2
Pure CNT	2.561	0.0178	1	0.721	0.0648	0.9697
10% Fe+ CNT	3.974	0.0194	0.999	0.703	0.0742	0.9879
10% Al+ CNT	3.620	0.00934	0.998	1.4712	0.0337	0.9361
10% Ag+ CNT	2.764	0.0154	0.9998	0.5611	0.0646	0.8891
10% Cu+ CNT	2.2776	0.0274	1	0.956	0.0643	0.9906

It can be seen from Table 4.3 and Table 4.4 that for both impregnated AC and impregnated CNT, pseudo 2nd order gave more accurate curve fitting by giving correlation factor close to unity as compared to 2nd order kinetic model. So it can be concluded that pseudo 2nd order is better kinetic model then 2nd order kinetic model.

CHAPTER 5

CONCLUSION AND RECOMENDATIONS

Ammonia, a chemical which can be a potential pollutant in water if exceeds certain limit. This research was done to investigate and reduce adverse effect of ammonia in industrial wastewater and to minimize it to the level which can be safe for human and marine life. To remove it, modified activated carbon and modified carbon nanotubes in different metal impregnations were studied. Furthermore, two different percentage loading of metals (1% and 10%) were investigated to compare result with pure form.

Different parameters were varied to see the effect on removal efficiency. Changing one parameter and keeping others constant, allow us to study the sole effect of that parameter. Among those parameters pH, agitation speed, dosage of adsorbent, contact time and temperature were considered. Each parameter was optimized before investigating other parameter. Among many available techniques for ammonia detection, ammonia detection electrode technique was used to identify the correct concentration of ammonia before and after the treatment.

For comparison of impregnating effect on CNTs and activated carbon, they were doped and decorated with 4 different metals including Al, Ag, Fe and Cu in 2 different loading percentage 1% and 10%. The results were than compared with pure state to study the impregnation effect on removal.

From the result obtained from pH variation, it was noticed that there was no effect of pH on the adsorption behavior, because of that it was concluded that the ammonia removal is not a function of pH. This study was done for both CNT and AC, but the result was same for both materials. When the temperature was investigated and it was allowed to increase from 25℃ to 70℃, it was clear from the observation that it increases the removal of ammonia. When the temperature was raised to 70℃ for 1g activated carbon, the removal efficiency increased to 43.3% but for CNT the removal was lower which was around 18%. Aluminum impregnation with 10% loading gave the highest result in case of AC. From that observation it was concluded that ammonia removal is a function of temperature.

Same phenomenon was observed when dosage of adsorbent was increased for fixed volume. As the dosage of adsorbent increases, the removal efficiency increases. When the dosage was increased to 2 g, the removal efficiency increases to 40% in case of 10% loading of aluminum metal impregnated on AC followed by Fe metal. Similar trend was observed in case of CNT impregnated with difference of low removal. It is due to the fact that more the adsorption sites, more chances of ammonia molecules to attach with the AC and CNTs surface.

Form the results, I concluded that Al gave the best results in both the loading percentages and for both adsorption materials (AC and CNT). Followed by Fe and then Cu. Ag gave quite low values of removal percentage. Among the loading ration, the results were according to expectation that 10% loading gave better removal results than 1%. And among the adsorption materials, Activated Carbon gave better result than CNT.

From the results, shown in result and discussion chapter, I conclude that the adsorption technique is not a good method for the removal of ammonia from wastewater. Many conventional methods give better results that adsorption technique. So the adsorption technique can be considered as a pre-treatment technique because of its economic viability.

Every experiment opens a new door for exploration and investigation. In this set of experiments, metal oxides were used to see the removal effect. For future study, we can extend this investigation a step ahead and include metal carbides and metal nitrides which might be effective. Similarly other metals like Zn, Ti etc. can also be a part of this study and give broader data for comparison.

Carbon has unique properties which vary from one of its allotropes to another. In this study Carbon Nanotubes and Activated Carbon were investigate. Fly Ash and Carbon Nanofibers can also be used to remove ammonia from water.

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APPENDICES

APPENDIX A

Experimental Results

Table A.1 Ammonia Removal % by Activated Carbon (Contact Time variation)

1% Impregnated Material Results

Time	Dosage	Agitation speed	Temp.	Pure	1% Fe+AC	1% Al+AC	1% Ag+AC	1% Cu+AC
(min)	(g)	(RPM)	(℃)	Removal %	Removal %	Removal %	Removal %	Removal %
30	1	200	25	1.6	8.4	8	4.9	7.6
60	1	200	25	4.5	14.6	13	12.1	11
120	1	200	25	5.3	15.7	14	13.5	12.1
240	1	200	25	8	18.1	17	16	15
1440	1	200	25	8.4	18.7	17.6	16.9	16

10% Impregnated Material Results

Time	Dosage	Agitation speed	Temp.	Pure	10% Fe+AC	10% Al+AC	10% Ag+AC	10% Cu+AC
(min)	(g)	(RPM)	(℃)	Removal %	Removal %	Removal %	Removal %	Removal %
30	1	200	25	1.6	16.7	12	8	8
60	1	200	25	4.5	17.7	15	14	13
120	1	200	25	5.3	20.8	18	17	15
240	1	200	25	8	20.8	20	19	18
1440	1	200	25	8.5	20.9	20.2	20	19.2

Table A.2 Ammonia Removal % by Activated Carbon (Dosage variation)

1% Impregnated Material Results

Dosage	Time	Agitation speed	Temp.	Pure	1% Fe+AC	1% Al+AC	1% Ag+AC	1% Cu+AC
(g)	(hr)	(RPM)	(℃)	Removal %	Removal %	Removal %	Removal %	Removal %
0.05	2	200	25	0	2.1	4.1	4.1	0.4
0.1	2	200	25	1.7	7.6	6.4	5.7	0.8
0.5	2	200	25	5.3	8.7	10.2	9.1	4.1
1	2	200	25	9.1	10.6	16.7	10.6	9.9
1.5	2	200	25	12	17.1	26.5	13.5	18.8
2	2	200	25	15.3	20.4	31.5	18.1	22.1

10% Impregnated Material Results

Dosage	Time	Agitation speed	Temp.	Pure	10% Fe+AC	10% Al+AC	10% Ag+AC	10% Cu+AC
(g)	(hr)	(RPM)	(℃)	Removal %	Removal %	Removal %	Removal %	Removal %
0.05	2	200	25	0	2.9	0	2.1	0.4
0.1	2	200	25	1.7	5.7	0.8	2.8	3.3
0.5	2	200	25	5.3	14.9	11.7	3.7	10.6
1	2	200	25	9.1	20.4	21.4	7.2	21.8
1.5	2	200	25	15.3	30.9	32.9	8.7	24.9
2	2	200	25	15.3	37.8	40.3	10.2	33.5

Table A.3 Ammonia Removal % by Activated Carbon (Agitation Speed variation)

1% Impregnated Material Results

Agitation speed	Time	Dosage	Temp.	Pure	1% Fe+AC	1% Al+AC	1% Ag+AC	1% Cu+AC
(RPM)	(hr)	(g)	(℃)	Removal %	Removal %	Removal %	Removal %	Removal %
100	2	1	25	9.2	12.7	16.3	12	13.4
150	2	1	25	10.1	13.6	17.9	13.2	14.2
200	2	1	25	10.8	14.2	18.6	13.9	15
250	2	1	25	11.2	14.8	18.9	14.2	15.8

10% Impregnated Material Results

Agitation speed	Time	Dosage	Temp.	Pure	10% Fe+AC	10% Al+AC	10% Ag+AC	10% Cu+AC
(RPM)	(hr)	(g)	(℃)	Removal %	Removal %	Removal %	Removal %	Removal %
100	2	1	25	9.2	12.7	16.3	12	13.4
150	2	1	25	11	13.9	17	13	14
200	2	1	25	12	14.2	17.8	13.8	15.6
250	2	1	25	12.2	14.4	18	14.1	15.9

Table A.4 Ammonia Removal % by Activated Carbon (Temperature variation)

1% Impregnated Material Results

Temp.	Time	Dosage	Agitation Speed	Pure	1% Fe+AC	1% Al+AC	1% Ag+AC	1% Cu+AC
(°C)	(hr)	(g)	(RPM)	Removal %	Removal %	Removal %	Removal %	Removal %
25	2	1	200	9.2	9.1	10.6	16.7	10.6
50	2	1	200	10.1	19.1	25	28.9	17.1
70	2	1	200	10.8	23	26	32	19

10% Impregnated Material Results

Temp.	Time	Dosage	Agitation Speed	Pure	10% Fe+AC	10% Al+AC	10% Ag+AC	10% Cu+AC
(°C)	(hr)	(g)	(RPM)	Removal %	Removal %	Removal %	Removal %	Removal %
25	2	1	200	9.1	20.4	21.4	7.2	15
50	2	1	200	19.1	28	32.4	17.4	22
70	2	1	200	23	37.8	40	19.8	28

Table A.5 Ammonia Removal % by CNTs (Contact Time variation)

1% Impregnated Material Results

Time	Dosage	Agitation speed	Temp.	Pure	1% Fe+CNT	1% Al+CNT	1% Ag+CNT	1% Cu+CNT
(min)	(g)	(RPM)	(℃)	Removal %	Removal %	Removal %	Removal %	Removal %
30	1	200	25	8	9.2	9.5	7.8	8.9
60	1	200	25	9.4	10.1	10.2	8.2	10.5
120	1	200	25	10.3	11.5	11	8.9	11.4
240	1	200	25	11.3	15.6	15.6	10.8	13.8
1440	1	200	25	12	16.6	16.4	12.4	14.8

10% Impregnated Material Results

Time	Dosage	Agitation speed	Temp.	Pure	1% Fe+CNT	1% Al+CNT	1% Ag+CNT	1% Cu+CNT
(min)	(g)	(RPM)	(℃)	Removal %	Removal %	Removal %	Removal %	Removal %
30	1	200	25	8	10.4	11.5	8.2	10.5
60	1	200	25	9.4	11.2	12.3	9.1	11.9
120	1	200	25	10.3	12.6	13.4	9.8	13.1
240	1	200	25	11.3	16.4	16.8	11.5	15.4
1440	1	200	25	12	17.3	18.4	12.6	16.8

Table A.6 Ammonia Removal % by CNTs (Dosage variation)

1% Impregnated Material Results

Dosage	Time	Agitation speed	Temp.	Pure	1% Fe+CNT	1% Al+CNT	1% Ag+CNT	1% Cu+CNT
(g)	(hr)	(RPM)	(℃)	Removal %	Removal %	Removal %	Removal %	Removal %
0.05	2	200	25	7.2	6.9	7	8.7	8.7
0.1	2	200	25	8.7	9	8	8.7	10.6
0.5	2	200	25	9.5	10	9	8.7	10.6
1	2	200	25	10.3	11.5	11	8.9	11.4
1.5	2	200	25	10.3	12.5	13.9	9.9	13.5
2	2	200	25	10.6	14	14.3	10	14.3

10% Impregnated Material Results

Dosage	Time	Agitation speed	Temp.	Pure	1% Fe+CNT	1% Al+CNT	1% Ag+CNT	1% Cu+CNT
(g)	(hr)	(RPM)	(℃)	Removal %	Removal %	Removal %	Removal %	Removal %
0.05	2	200	25	7.2	7	7.2	7	4.1
0.1	2	200	25	8.7	7.8	7.2	8	6.8
0.5	2	200	25	9.5	9.5	10.2	8.9	7.6
1	2	200	25	10.3	12	12.5	9	11.4
1.5	2	200	25	10.3	15	16	10	14.3
2	2	200	25	10.6	17	18.8	10.2	14.8

Table A.7 Ammonia Removal % by CNTs (Agitation Speed variation)

1% Impregnated Material Results

Agitation speed	Time	Dosage	Temp.	Pure	1% Fe+CNT	1% Al+CNT	1% Ag+CNT	1% Cu+CNT
(RPM)	(hr)	(g)	(°C)	Removal %	Removal %	Removal %	Removal %	Removal %
100	2	1	25	10.1	10.8	13.8	8.5	11.6
150	2	1	25	10.5	11.4	14.8	9.5	12.6
200	2	1	25	11.1	11.9	15.3	10.1	13.1
250	2	1	25	11.4	12.2	15.8	10.6	13.6

10% Impregnated Material Results

Agitation speed	Time	Dosage	Temp.	Pure	1% Fe+CNT	1% Al+CNT	1% Ag+CNT	1% Cu+CNT
(RPM)	(hr)	(g)	(°C)	Removal %	Removal %	Removal %	Removal %	Removal %
100	2	1	25	10.1	13	15.1	9.1	13.1
150	2	1	25	10.5	14.2	16.2	10.5	14.2
200	2	1	25	11.1	15.1	16.8	10.9	14.8
250	2	1	25	11.4	15.4	17.1	11.2	15.3

Table A.8 Ammonia Removal % by CNTs (Temperature variation)

1% Impregnated Material Results

Temp.	Time	Dosage	Agitation Speed	Pure	1% Fe+CNT	1% Al+CNT	1% Ag+CNT	1% Cu+CNT
(°C)	(hr)	(g)	(RPM)	Removal %	Removal %	Removal %	Removal %	Removal %
25	2	1	200	10.3	10	9	8.9	9.5
50	2	1	200	11	12	11	10	10.5
70	2	1	200	12	16	13	11	12

10% Impregnated Material Results

Temp.	Time	Dosage	Agitation Speed	Pure	1% Fe+CNT	1% Al+CNT	1% Ag+CNT	1% Cu+CNT
(°C)	(hr)	(g)	(RPM)	Removal %	Removal %	Removal %	Removal %	Removal %
25	2	1	200	10.3	12	12.5	9	11.4
50	2	1	200	11	13	13	10.5	12
70	2	1	200	12	17.4	16	12	15

APPENDIX B

Table B.1: Calculation of the Chemical Materials

- Iron (Fe) oxide was prepared from ferric nitrate [$Fe(NO_3)_3.9H_20$)]

$$\frac{404\ (\frac{g}{mol})}{x} = \frac{56\frac{g}{mol}}{0.2\ (g)}$$

$$x = 1.442g\ of\ [Fe(NO_3)_3.9H_20)]$$

- Aluminum (Al) oxide was prepared from aluminum nitride $[Al(NO_3)_3.9H_2O]$

$$\frac{375\ (\frac{g}{mol})}{x} = \frac{27\frac{g}{mol}}{0.2\ (g)}$$

$$x = 2.77g\ of\ [Al(NO_3)_3.9H_2O]$$

- Silver (Ag) oxide was prepared from silver nitrate $[AgNO_3]$

$$\frac{169.87\ (\frac{g}{mol})}{x} = \frac{107.8\frac{g}{mol}}{0.2\ (g)}$$

$$x = 0.3151g\ of\ [AgNO_3]$$

- Copper (Cu) oxide was prepared from copper (III) nitrate $[Cu(NO_3)_2.3H_2O]$

$$\frac{241.6\ (\frac{g}{mol})}{x} = \frac{63.546\frac{g}{mol}}{0.2\ (g)}$$

$$x = 0.760g\ of\ [Cu(NO_3)_2.3H_2O]$$

APPENDIX C

Table C.1: Materials for Experiment

No.	Materials
1	Sample Adsorbents o Raw Activated Carbon o Raw CNTs
2	Stock Ammonia Solution
3	1.0 M Sodium Hydroxide
4	1.0 M Nitric Acid
5	Ammonium Chloride (NH_4Cl)
6	10 N NaOH
7	Deionized Water
8	Ethanol (Purity 98%)
9	Ferric Nitrate
10	Aluminum Nitride
11	Silver Nitrate
12	Copper (III) Nitrate

APPENDIX D

Table D.1: Equipments for the Experiments

No.	Equipments
1	Thermo Gravometric Analysis (TGA)
2	Scanning Electron Microscopy (SEM)
3	Energy Dispersive X-Ray Spectrometry (EDX)
4	Ammonia Selective Electrode
5	Mechanical Shaker
6	Nano Coating Machine
7	Magnetic Stirring Heater
8	Sonicator
9	Balancer
10	pH indicator
11	1000 ml Volumetric Flask
12	125 ml Conical Flask
13	100 ml Beaker
14	Furnace

APPENDIX E

Experimental Figures

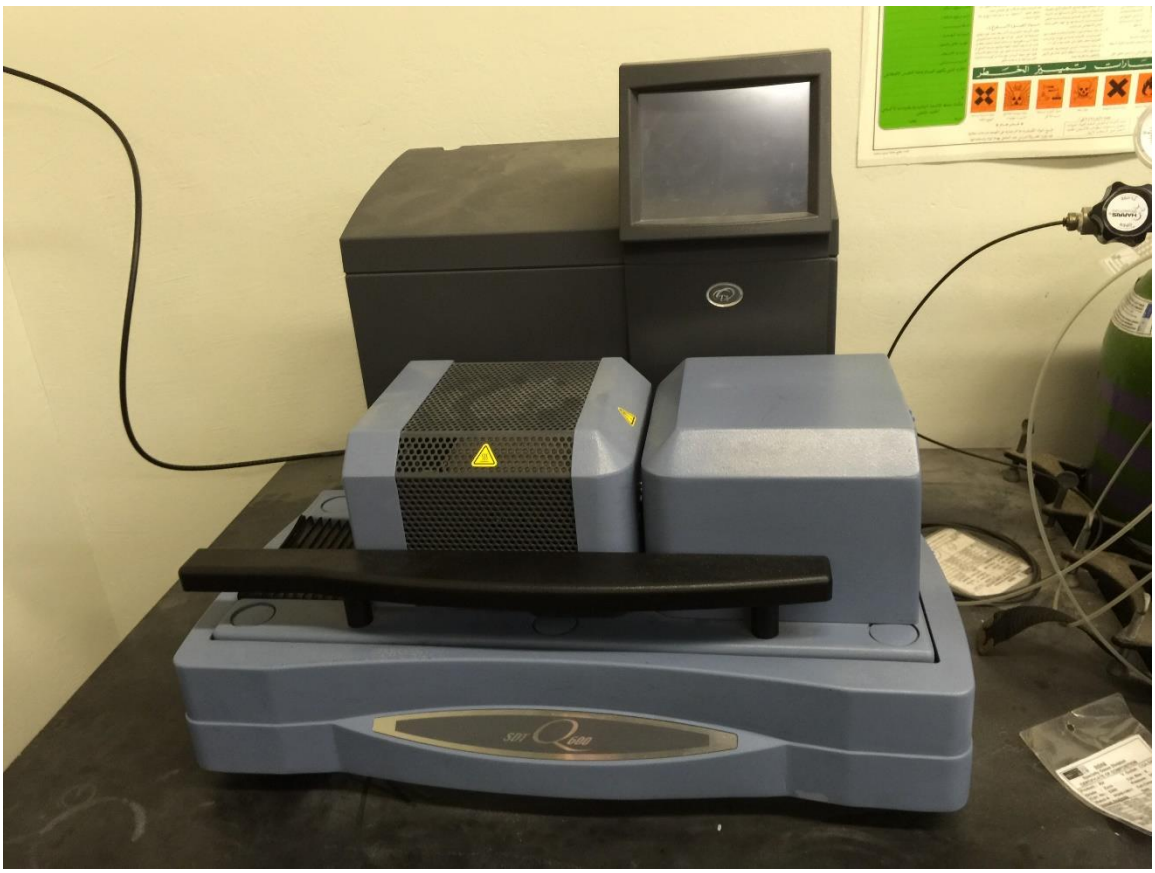

Figure E.1 Photograph of TGA instrument

Figure E.2 Photograph of Mechanical Shaker

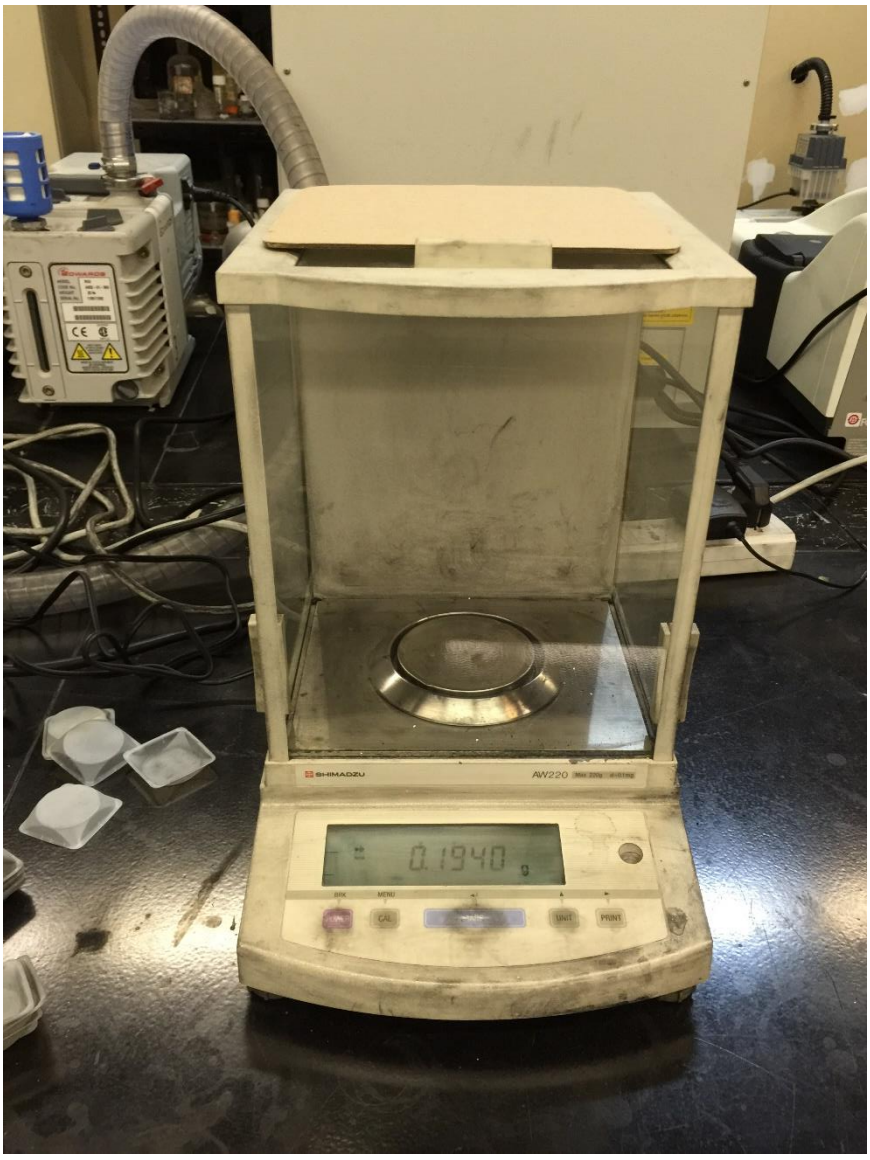

Figure E.3 Photograph of Weighing Balance

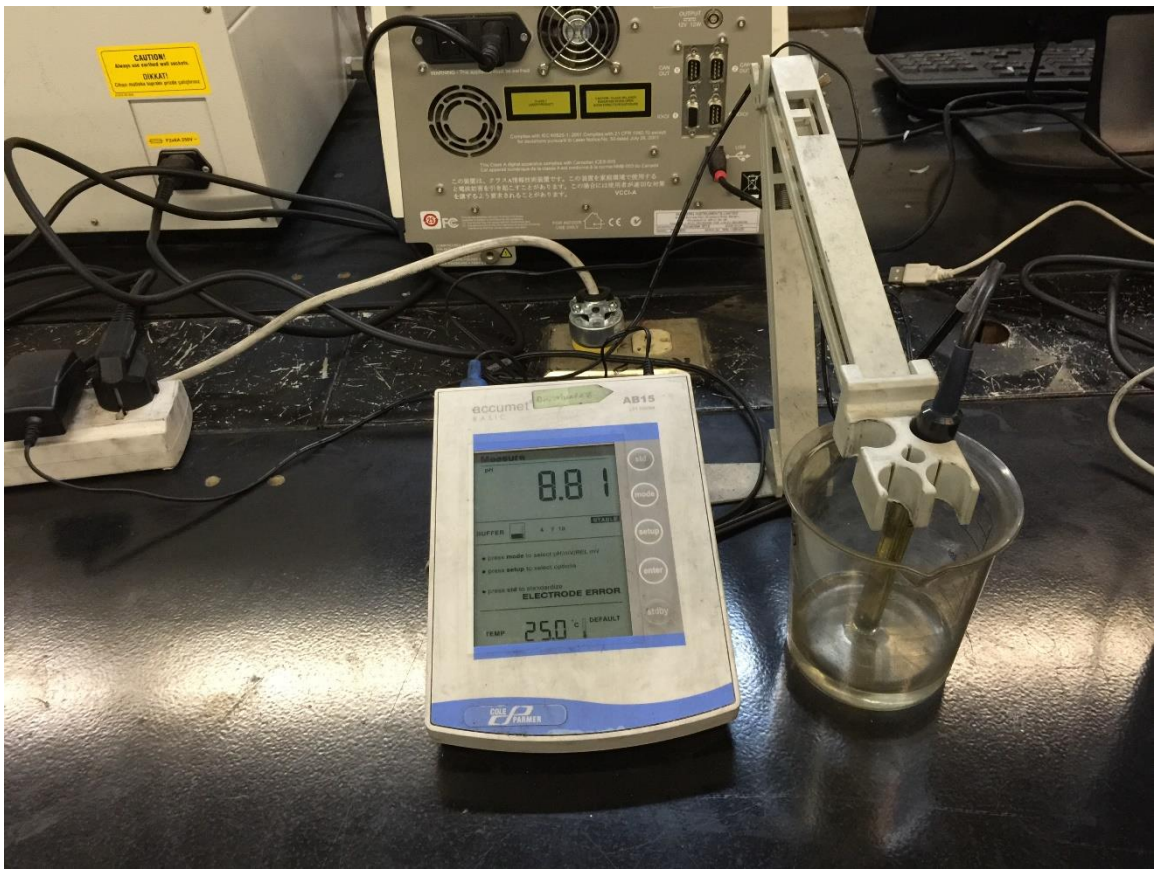

Figure E.4 Photograph of pH Meter

Figure E.5 Photograph of Nano Coating Machine

Figure E.6 Photograph of Deionize water instrument

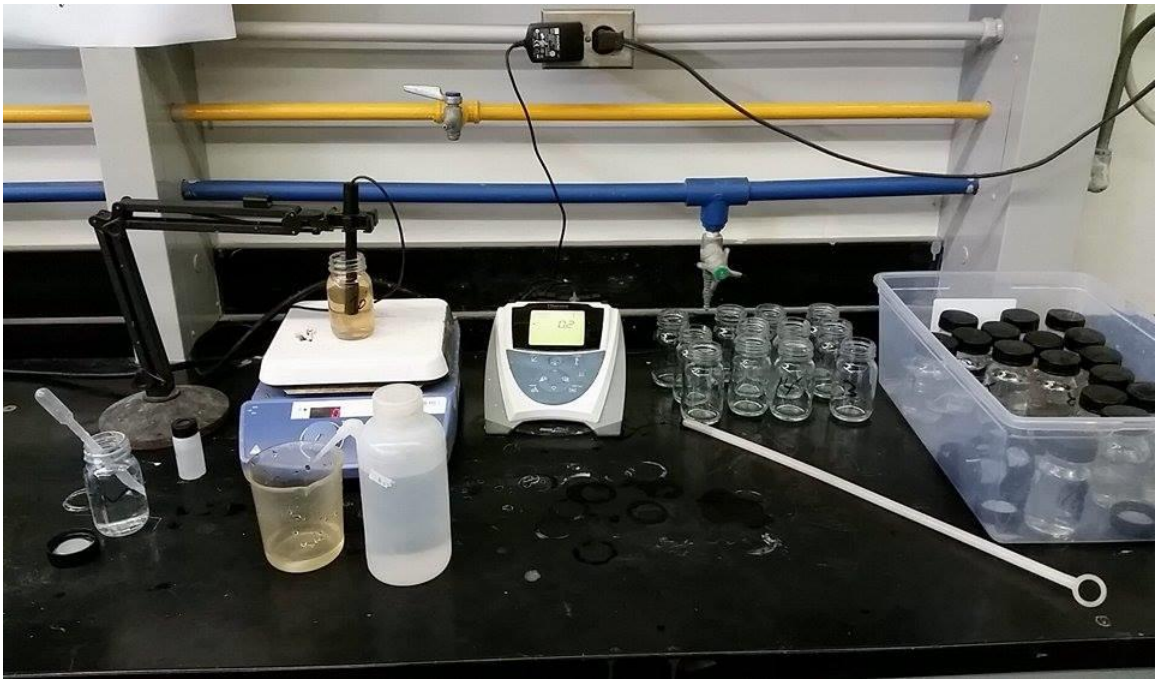

Figure E.7 Photograph of Experiment Setup

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